

STUDIES ON DE-OILING AND CHLORINATION OF SLACK WAX

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

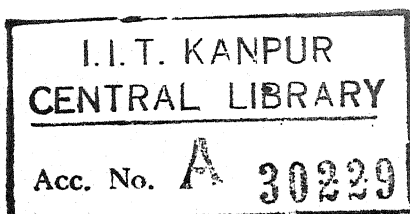
By
ASHOK KUMAR DHINGRA

to the

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
AUGUST 1974

✓
CME-1974-M-DHI-STU

Thesis
665.4
D537



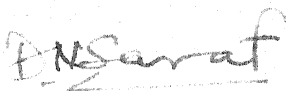
13 SEP 1974

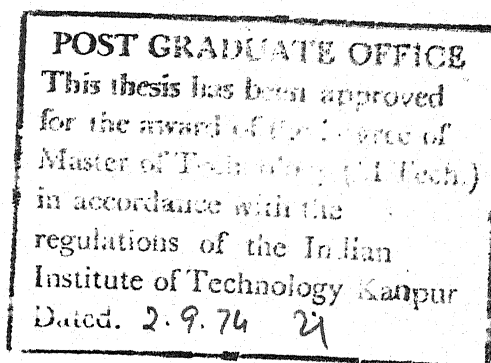


CERTIFICATE

This is to certify that the present work "STUDIES ON THE DE-OILING AND CHLORINATION OF SLACK WAX" has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

August 12, 1974


(Dr.) D.N. Saraf
Associate Professor
Department of Chemical Engg.
Indian Institute of Tech.
Kanpur-208016, India



ACKNOWLEDGEMENTS

The author expresses his deep sense of gratitude and indebtedness to Dr. D.N. Saraf for his valuable guidance and constant encouragement throughout this work.

The author also wishes to extend his sincere thanks to Professor K.K. Sirkar for his helpful discussions during the progress of the project.

The help given by Mr. Subhash Bhatia, N.K.Agrawal and other friends shall be remembered with gratitude. The author is thankful to Mr. B.S. Pandey for typing the manuscript.

Author

CONTENTS

	List of Tables	v
	List of Figures	vi
	Abstract	vii
CHAPTER		
I	INTRODUCTION	1
	De-Oiling Slack Wax	4
	Chlorination of Paraffin Wax	8
	Analysis of Paraffin Wax	10
II	LITERATURE REVIEW	14
	A. De-Oiling	14
	B. Chlorination of Paraffin Wax	19
III	EXPERIMENTAL SET UP AND PROCEDURE	23
	A. De-Oiling	23
	B. Chlorination	27
IV	PRODUCT TESTING PROCEDURES	31
V	SELECTION OF DE-OILING SOLVENTS	40
VI	RESULTS AND DISCUSSIONS	43
VII	CONCLUSIONS AND RECOMMENDATIONS	61
	REFERENCES	64
APPENDIX		
A	Calculation of Oil Content (wt.%) in Wax	67
B	Calculation of Chlorine content (wt.%) in CPW	69
C	Calculation of Viscosity of CPW	70
D	Economics of the Process	71

...

LIST OF TABLES

TABLE	CAPTION	PAGE
1	Slack Wax Production and Potential Sources in India 	3
2	Analysis of Paraffin Wax of Melting Point 58°C 	10
3	Solubility of Paraffin Wax in Various Solvents and Approximate Cost of Solvents	41
4	Pressing Time Versus Solvent to Slack Wax Ratio by Weight 	49

* * *

LIST OF FIGURES

FIGURE	CAPTION	PAGE
1	Schematic Diagram of the De-Oiling Equipment	26
2	Schematic Diagram for the Experimental Set-up (Chlorination) ...	30
3	Apparatus for Determining the Oil Content in Waxes	33
4(a)	Percentage Oil (by weight) in Scale Wax versus Solvent to Slack Wax Ratio	46
4(b)	Yield of Scale Wax versus Solvent to Slack Wax Ratio	47
4(c)	Solvent Retention in De-Oiled Wax versus Solvent to Slack Wax Ratio ...	48
5(a)	Chlorine Content in CPW, Wt.% versus Chlorination Time at Different Temperatures	55
5(b)	Chlorine Content (% wt.) in CPW Versus Viscosity	56
5(c)	Shear Stress versus ShearRate of CPW	57
5(d)	Chlorine Content (% by wt.) in CPW versus Refractive Index	58
5(e)	Chlorine Content in CPW, wt. % versus Density of CPW	59

* * *

ABSTRACT

Solvent de-oiling of slack wax (melting point 56-60°C, oil content about 13.6% by weight), supplied by Barauni Refinery was undertaken to get pure paraffin wax. This was chlorinated to get chlorinated paraffin wax (CPW), which is used as a plasticizer for PVC and is mostly imported at present.

For de-oiling, three solvents, Methyl Iso Butyl Ketone (MIBK), Ethylene Dichloride and Ethylene Dichloride + Methylene Dichloride were tried, varying the slack wax to solvent ratio. MIBK was found to be the best de-oiling solvent and three times of this solvent at 5°C gave a scale wax with less than 0.5 percent oil by weight. The yield of scale wax obtained was 80% by weight of slack wax. The scale wax was purified by passing through a silica gel column and a sufficiently good colored paraffin wax was obtained.

The purified scale wax, obtained from de-oiling experiments was chlorinated at $75 \pm 2^\circ\text{C}$ and $85 \pm 2^\circ\text{C}$, at a fixed chlorine gas flow rate of 0.3 lits/min.kg. of wax, in a batch reactor.

To reach 40 weight percent chlorine content in the chlorinated paraffin wax (CPW) it took about 38 hours when reaction was carried out at 75°C. Although the reaction time was reduced to 30 hours at 85°C but the color of the product was much poorer. Barium stearate when used as catalyst reduced the reaction time from 38 hours to 26 hours with additional advantage of improved color.

...

CHAPTER I

INTRODUCTION

The availability of surplus slack wax and the shortage of paraffin waxes in India provides incentive to develop economic and efficient techniques of converting the former into the latter. Paraffin waxes have excellent moisture-vapor, water resistance, chemical inertness and freedom from odour, color and taste properties. They can be used in all types of food packaging, in drugs, medicaments, cosmetics, in paper industry for paper coatings, in match industry and various others (1). In view of the heavy return they offer in terms of investment, technologists and refiners are concentrating more and more on the production and various end uses of paraffin waxes. Lately paraffin waxes have found many intermediate uses. They are being used as a starting material for chemical processing to chlorinated products, fatty acids, lubricating oils, setting point depressants etc.

The chlorinated paraffin waxes (41 to 43% chlorine by weight) have found numerous uses, mainly in the plastic industry as a plasticizer, or to be exact as an extender used with Di-octyl phthalate (DOP) in the processing of vinyl polymers, polystyrene and others. An extender is a material which although not a true plasticizer, increases the efficacy of the normal plasticizer, enabling these usually expensive

chemicals to be used in small quantities. Also because of their viscous nature, their compatibility with oils and gradual liberation of HCl at high temperature; chlorinated paraffin waxes are particularly effective as extreme pressure lubricant additives. In the textile industry, chlorinated paraffin waxes are used as flame proofing agents and in the electrical industry in the manufacture of di-electric fluids and insulating covering materials for electrical conductors. Lot of research is being done on the various end uses of chlorinated paraffin waxes. They have been successfully used in Flameproof electrical cables (2), in making cleaning paste for floors (3), in giving a bright glossy coating and desirable pick characteristics to paper (4), flame-proof paper (5), adhesive sticks (6) etc. It seems that this chemical has endless uses specially in consumer goods. But most of the chlorinated paraffin waxes used in India, are being imported at present.

The consumption of paraffin waxes has been increasing steadily (from about 18,000 tons in 1960, it increased to about 27,000 tons in 1965 and about 39,000 tons in 1970) but the production has remained more or less steady at 38,000 tons/annum level. Thus from an exporters status (in 1960 about 20,000 tons of paraffin wax was exported, the export fell in 1965, to 11,280 tons and in 1968, it reached about 2950 tons), India has become an importer of different waxes (in 1970,

about 1000 tons of wax costing about 26 lacs rupees was imported) (7). The consumption is expected to further rise sharply.

The major source of getting pure grades of paraffin waxes is from slack wax, which is obtained during dewaxing to get lube oil. This may contain 10 to 50% oil and is soft or semi solid. The crude oil from Assam is relatively rich in paraffin waxes and it is desirable to separate these waxes before processing. From these two sources, we are getting enough slack wax, but for a good and economical de-oiling process, we are not in a position to boost up our production of paraffin waxes. In India, the widespread use of slack wax is as a fuel.

Table 1 gives the position of slack wax in India in 1971 (8):

Table 1

Slack Wax Production and Potential Sources(8)

<u>Source</u>	<u>Slack wax production (tons/year)</u>
Barauni	60,000
Haldia	50,000
Madras	60,000
Bombay	35,000

Madras refinery has undertaken de-oiling of slack wax using the costly MEK (methyl ethyl ketone) process on a small scale. This solvent is being imported at present.

Clearly there is a need for workable technology for utilization of surplus slack wax into more useful products.

De-Oiling Slack Waxes:

The wax de-oiling operations are similar to those used in de-waxing oils and often vary in the choice of treating conditions. The commercially exploited processes for the manufacture of paraffin waxes are as follows:

1. Sweating: Sweating is a fractional melting method for separating oil from wax. It consists in heating and transferring the liquified slack wax into large pans, where the wax is chilled to form a solid cake. The temperature is then raised gradually and the liquified portions are removed from the pans. The sweating pans are usually 20 to 60 feet long, 8 to 10 feet wide and about 8 inches deep. The wax cake is about 6 inches thick. The cake is supported on wire screens and provisions are made for the free draining of liquefied fractions. Cooling and heating is effected by passing cold or hot water through the coils, which are located above the screens supporting the wax cake but below the surface of the cake (9).

The pans are filled with water in the depth just sufficient to cover the screen. The molten slack wax is pumped into the pans until the desired thickness of the wax cake is obtained. The wax is solidified by pumping cold water through the coils.

After a solid wax cake is formed, water is drained from the bottom of the pans, and the cake is allowed to rest on the screens. The cake is heated gradually by circulating warm water through the coils or by heating the chamber or "oven" where the pans are located with the special steam coils outside the pans. The two heating methods may be combined.

The rate of heating the cake is very important to obtain the best separation between oil and wax. In commercial practice the rate of heating is usually 1-2°F/hr. Sufficient time must be allowed to drain the successive portions of liquified materials.

The drippings from the pans are collected in two fractions. The first fraction contains oil and low melting point waxes and is known as "foot oil". The second or "intermediate cut" contains little oil but large quantities of low melting point waxes and appreciable quantities of high melting point waxes.

The "intermediate cut" is usually reblended with the fresh slack wax and a very complicated system of recycling and splitting the intermediate cut into several fractions is employed to increase the yield of wax and to obtain waxes of different melting points.

The wax remaining on the pan and the various cuts are refined with chemicals like H_2SO_4 , NaOH and clay to make it

completely transparent, tasteless and odourless.

The theory behind this process is that paraffin wax when allowed to cool, can crystallize in plates, needless or crystalline form with crystals indifferently attached. It has been found that if the wax crystallizes in the needle form the oil can drip through the intermediate spaces much more easily, than if the wax crystallizes in plate or crystalline form. This makes the rate of cooling very important during sweating.

The yield of sweated wax varies from 20% to 65% depending upon the initial oil content of slack wax and the operating conditions. The oil content in good quality sweated wax, may be as low as 0.1%.

2. Solvent Pressing: To-day, by far the greatest amount of de-oiling is carried out by means of solvents. In principle, this procedure consists in dissolving the slack wax in a suitable solvent and then subjecting it to a crystallization process by cooling, the wax separating in crystalline form and oil along with solvent dripping through. The whole mixture is pressed and thus wax is freed from the oil and solvent. The solvent oil mixture is distilled and we get lubricating stock which is an important product, and the solvent which is recycled back.

Special requirements are set for the solvent. The solvent should be cheap and easily available, must not possess

a corrosive action, it should not be highly poisonous, it must be volatile with steam and easily separable from water and must not react with water. It must be completely miscible with the oil at 30°C and must still dissolve the oil readily at -30°C (10). A good de-oiling solvent should also have the lowest possible solubility for wax, since a solvent with low wax solubility, will permit de-oiling at higher temperatures with consequent saving in refrigeration costs and also the lubricating stock obtained will be completely free from wax, otherwise even one percent of paraffin wax in lubricating oil, can cause it to get at temperatures as high as 5-10°C thus increasing its pour point. A common dewaxed oil should have a pour point of -30°C.(11).

Various de-oiling solvents have been used to get pure paraffin waxes. Acetone (14), Benzene and Acetone (15), MEK + Benzene, Acetone + Benzene (16), Ethylene Dichloride, Methylene Dichloride (17), have all been used successfully to de-oil slack waxes.

The use of single solvents eliminates the necessity of adjusting the solvent composition and often simplifies the solvent recovery problem. However, the solubility characteristics of single solvents are inflexible and can be controlled only by varying the solvent to oil ratio and the temperature.

The solubility characteristics of mixed solvents can be controlled by one more variable: solvent composition. Mixed solvents normally contain two components which differ in their solvent characteristics. One of the components is often referred to as "wax precipitator" and the other as "dissolver" (18). The "wax precipitator" solvents like acetone, ketones, chlorinated methanes and ethanes; are completely miscible with oil in all proportions. The "dissolver" like benzene keeps the oil in solution. It dissolves practically no wax, but adds to the filtration rate. The quantities of the two components in mixed solvents are adjusted to obtain the best possible blend for de-oiling purposes.

Chlorination of Paraffin Wax:

Chlorinated paraffin waxes are produced by passing gaseous chlorine into the paraffinic hydrocarbon at a temperature at which the viscosity of the paraffin is sufficiently low to permit free evolution of the hydrogen chloride and unreacted chlorine (19). Catalysts are generally not required, but the reaction is carried out in the presence of light. Chlorination in the dark is sometimes accompanied by side reactions which cause discoloration of the product.

Girelli and Siniramad (18) in their study of the effects of chlorine flow rate and temperature on the yields and properties of the chlorinated paraffin waxes found, that with a paraffin wax of 48°C melting point, a maximum rate of

chlorine absorption was reached at 100°C, and that the color of the product became darker with increasing temperature. They concluded from their experiments that the optimum flow rate and temperature for the particular paraffin wax they were using were 28 liters Cl_2 /hr(kg paraffin) and 80°C, respectively. Variation of these two, conditions using the same paraffin wax, resulted in products of different color and viscosity.

As will appear from the above discussion, the process variables change with the wax used and the properties of chlorinated product required. And therefore, there can not be one standard process of paraffin wax chlorination. Commercial paraffin wax is not entirely n-paraffin type, but also contains branched chain paraffins, cycloparaffins and others. A typical analysis of a paraffin wax, with m.pt. 58°C, refractive index at 80°C of 1.4302, oil content 0.2%, prepared in the laboratory by solvent recrystallization from a commercial sweated paraffin wax is given in Table 2 (20). It will be clear from this table, that it is not easy to attempt a kinetic study of the chlorination process, using a commercial grade paraffin wax, and no study upto date has been conducted. Also, the properties of paraffin wax, even with the same melting point vary widely depending upon their sources.

The general reaction mechanism of chlorination process is as follows:

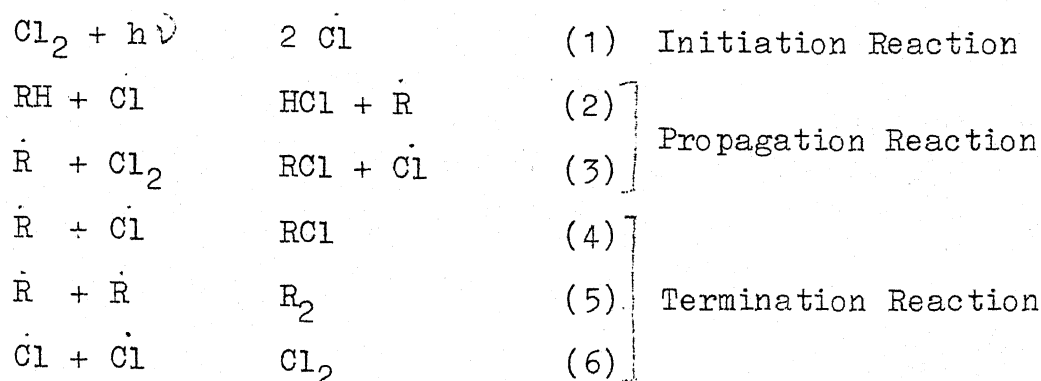
TABLE 2

Analysis of Paraffin Wax of m.pt. 58°C (20)

No. of c atoms	% of Normal Paraffin	% of Iso Paraffin	% of Cyclo Paraffin	% of Alkyl Benzene
16	-	-	-	-
17	-	-	-	-
18	-	-	-	-
19	-	-	-	-
20	-	-	-	-
21	0.2	-	-	-
22	1.0	-	-	-
23	2.8	-	-	-
24	5.2	-	-	-
25	7.3	-	-	-
26	9.2	-	0.4	-
27	10.5	-	0.9	-
28	10.1	-	1.3	-
29	9.8	0.3	1.5	-
30	7.6	0.6	1.7	-
31	6.5	1.0	1.7	-
32	4.4	0.9	1.7	-
33	3.0	1.0	1.3	0.1
34	1.9	0.7	1.0	-

Table 2 (contd)

35	1.0	0.7	0.8	0.1
36	0.4	0.4	0.3	-
37	0.2	0.2	0.2	-
38	-	-	-	-
39	-	-	-	-
40	-	-	-	-
Total	<u>81.1</u>	<u>5.9</u>	<u>12.8</u>	<u>0.2</u>
		100.0%		



Several patented variants (42, 43, 44, 46) of the chlorination process use different temperatures for progressive stages of chlorination. The Diamond Alkali Co process introduces the first 33% chlorine at less than 90°C and completes the chlorination at slightly higher temperature - but less than 100°C. In a Japanese process (35) chlorination is begun at 70°C and progressively raised to 150°C, over a period of 24 hrs. This process employs calcium aleate or benzoate as catalyst.

The present investigation was undertaken to study the feasibility of production of paraffin wax from slack wax, obtained from Barauni Refinery, using solvents and further chlorination of de-oiled slack wax (scale wax) to get chlorinated paraffin wax (of about 40% chlorination), suitable as a plasticizer for PVC.

The feasibility study includes the following important aspects:

- A. De-Oiling: 1. Preliminary design of a laboratory scale de-oiling equipment.

2. Finding the most economical solvent, along with the optimum operating conditions.

- B. Chlorination;
1. Preliminary design of a laboratory scale chlorination equipment.
 2. Study of chlorination reaction at different temperatures for scale wax and pure paraffin wax.
 3. Effect of catalyst on chlorination reaction.

* * *

CHAPTER II

LITERATURE REVIEW

A De-Oiling:

Mahrwald (21) has described the de-oiling of waxes by means of solvents. He opines that the process and the solvent to be used depends on the source of the raw material and the required purity of the final product. General rules can not be given. The old sweating process is not as favourable as de-oiling by selective solvents. In view of this and the fact that most of the published information on the de-oiling of slack wax is in the form of patents, it is difficult to give the chronological sequence of research done in this field, and it is more difficult to extract that information, which may be of use in de-oiling slack waxes from Indian sources. The best that can be done, is to list various solvents that have been used lately and the process modifications introduced.

2.1 Naphtha Pressing:

One of the early processes (12) involved mixing molten slack wax with naphtha, cooling to solidify the blend, cutting the solid into sheets and pressing to remove the oil naphtha solution.

The process was abandoned because of economic considerations. However, naphtha pressing employing modern equipments

and improved procedure is in limited use.

The quantity of naphtha used for solvent pressing of wax may vary from 0.5 to 1.5 volumes per volume of slack wax. The quantity of naphtha or for that matter any solvent required during de-oiling depends on the oil content and the operating variables such as temperature, pressure and filtration time. A small quantity of solvent is always retained by de-oiled wax and when this is distilled, the oil associated with the solvent will remain in the product. It is very difficult to separate lubricating oil and wax by distillation because both boil nearly in the same range. By solvent pressing, the yield is more than that obtained in sweating. In this case it is more than 65% by weight, but again depending upon the oil content in slack wax.

2.2 MEK De-Oiling:(Union Oil Co., California Process)

The method used in MEK de-oiling is first to chill the slack wax sufficiently to crystallize desired wax fractions, and then to add methyl ethyl ketone as a solvent for the oil and low melting point waxes which have not crystallized out during chilling (13).

The methyl-ethyl-ketone, oil-wax slurry is then filtered in a rotary type filter, repulped with fresh solvent and again filtered in a second rotary type filter to produce wax containing oil well below 0.5% by weight.

Solvent ratios on the feed entering the primary and secondary filters are approximately 3:1 MEK to feed and both filters are operated at the same temperature, from 20 to 24°C. The melting point of the wax produced may be controlled to a limited extent by controlling the chiller outlet and filter temperatures.

Solvent recovery from the wax and filtrate oil is accomplished by distilling off the MEK and then steam-stripping the wax and filtrate oil to remove any traces of MEK. With the introduction of steam into the system, some means must be provided to remove water from solvent because water concentration above 1% in the solvent prohibits proper de-oiling operations. Separation of water from the solvent is accomplished by utilizing the fact that a minimum boiling-point mixture of MEK and water occurs which consists of 90% MEK and 10% water.

2.3 Ethylene Di-Chloride as Solvent:

Fischer (22) has described a spray De-oiling process, which uses Ethylene Dichloride as the solvent. It produces an oil free wax by forming small wax particles within a stream of air and then dissolving the resulting oil film from the particles. The solvent to slack wax ratio used is 5:1 (by volume) and the de-oiled wax obtained has an oil content of 0.2% by weight. The temperature used is about 10°C and it has been claimed that the total loss of solvent is approximately 5 kg. per ton of slack wax (10% oil by weight) processed. The

advantages of using this solvent are: i) In the temperature range below 10°C , this shows a good solvency for the oils without dissolving appreciable amounts of waxes. As compared to MEK process, solvent losses in this process are less, because of its favourable b.pt. of 83.5°C . The yield of de-oiled wax, claimed is 70% by weight of slack wax.

An improvement on the above process, has been claimed by Westerhoff (23). According to him, prior to Spray De-oiling, the oil content in the slack wax can be decreased by pulverizing and stirring the slack wax in presence of 100% Ethylene Dichloride and 100% water and then filtering.

In a French patent (24), slack wax containing 30% by weight of oil is slurried in Ethylene Dichloride (using 4 times the volume of wax) and the slurry is then washed counter-currently at 0°C with 2-5 volumes of solvent. The de-oiled wax (0.3% oil by weight) is recovered by settling and draining or by filtration. The yield is 67% by weight.

Hoppe (25) used Ethylene Dichloride and Methylene Dichloride (1:1 by weight) to get de-oiled wax, by charging a mash container with a filter cake of 1 volume slack wax and 5 volumes of the above solvent at -20°C . Extra liquid solvent at 5°C and vaporized recovered solvent at 80°C were passed into the container to maintain the temperature at 5°C . The mixture was filtered to give a paraffin wax of oil content 0.3% by weight.

2.4 MIBK as Solvent:

According to Warnecke (26), significant advantages can be gained when the solvent for a wax de-oiling process is changed from MEK (Methyl-ethyl ketone) to MIBK (methyl isobutyl ketone). It is claimed that MIBK is as good a de-oiling solvent as MEK. And further the loss in solvent is less because of higher boiling point of MIBK and also it reduces the complexity of solvent recovery system.

In a recent U.S. Patent (27), the solvent used in de-oiling is a mixture of MEK and MIBK in the ratio 5:1 (solvent to slack wax) by volume. And in a later German patent (28), Harris has described a rotating vacuum filter, over which the solvent is sprayed and the entrapped oil from the wax cake is removed.

De-Colorization of De-Oiled Wax or Scale Wax:

The conventional method of decolorizing scale wax is by passing the molten scale wax through bauxite bed, heated to 80°C or above the melting point of scale wax. 5 tons of refined wax is obtained per ton of bauxite for dark crude waxes, to 60 tons for light colored waxes (30).

In a U.S. Patent (29), Mills has recommended, that colored paraffin waxes should be decolorized by diluting the wax with 1 to 10 volumes of a substantially non polar solvent, preferably 2,2,4, trimethyl-pentane or mineral spirits and then absorbing the impurities in an admixture of an acid activated adsorbed clay and one or more less acid adsorbent substances,

such as adsorbent carbon and adsorbent bauxite. This treatment, not only gives an improved color (ASTM color of < 1) but also results in a wax with practically no odor. Other adsorbent substances that have been used for decolorizing are silica gel, aluminium silicate, natural fuller's earth bleaching clay and crystalline zeolite molecular sieves (31). In a typical experiment using silica gel scale wax containing 1% oil by weight and 0.6% sulphur by weight was decolorized, by passing 40 parts of wax at 70°C through 1 part silica gel (previously heated for 3 hrs. at 160°C, average pore diameter 60 Å with particle size 0.25 to 0.5 mm).

Besides the above mentioned advances in the de-colorization of scale wax, the most commonly used process in industry is the Thermoform Continuous Percolator (32,33). In this process the regenerated adsorbent which is bauxite, is introduced from the top of the percolator (maintained at 65°C), where it flows down counter current to the charge (scale wax), which is introduced at the bottom. The de-colored product flows from the top of the percolator and goes to the "de-colorizer" column. The spent adsorbent flows as a slurry, to the wash column, where it is contacted by a counter current flow of naphtha to remove any oil, then dried in a heated vessel and finally regenerated by conventional means, and again fed to the percolator. A water white product, with an ASTM color index of < 1 is obtained.

B. Chlorination of Paraffin Wax:

Before 1858, according to Bolley (19), it had been a "dogma" among chemists that higher paraffins were unattacked by chlorine. He undertook a systematic study of the chlorination of higher paraffins, and concluded that an understanding of the action of chlorine on the higher paraffins, must await the results of comprehensive research on the nature of the paraffins themselves. It was left to Bohringer to develop a process for chlorinating the higher paraffins and he got it patented in 1910.

In the classic Bolley method, chlorine is passed through melted paraffin wax, until the desired chlorine content is reached. Hydrochloric acid is evolved as a by-product. While in the Bohringer process, Chlorine is conducted into a solution, or suspension of carbon-tetrachloride (19).

The chlorination of paraffin wax is a very slow reaction, specially beyond 20% chlorination. According to a U.S. patent (34), it is stated that for producing a chlorinated paraffin wax of about 40% chlorination by weight, the time required is of the order of 50-80 hours, when the temperature maintained is 85-90°C and the chlorine gas is introduced at a pressure of 10-25 lbs per square inch and a flow rate of 27 gms. /hr.kg of wax. To increase the reaction rate ultra-violet light of wavelength less than 3000 Å is suggested. Massaki Vokoyama (35) has shown that for the same temperature, same flow

rate and same reaction time percent chlorination increases from 28.49% in absence of ultra-violet light to 30.10% in presence of ultra-violet light. In another Japanese patent, Shimada (38), recommends, Barium stearate, calcium oleate and calcium benzoate as reaction catalysts to decrease the reaction time.

Quite frequently, the rate of chlorination is retarded as the degree of chlorination increases. This is because of the undesirable deposits which may be formed upon the walls and other surfaces of the reaction zone. These deposits come in the way of effective transmittence of light. It is commonly recognized that a primary cause for deposit formation and/or reaction retardation, may be traced to minor amounts of contamination present in the reaction system e.g. iron contamination. Iron contamination may enter the reaction zone in trace amounts with the feed, or be unexpectedly derived from other sources and have a marked influence on the course of chlorination reaction (37). Ferric chloride is formed within the reaction zone in trace amounts because of the presence of hydrochloric acid, chlorine and iron from the reaction vessel. Hull (38) has described a type of sludge produced by light of certain wavelengths, and the type of discoloration produced when iron reactors are used in the chlorination of paraffins. Ziolkowski (39) has given evidence of wall deposits in photochlorination of paraffins. Sometimes, he observed the coating directly

to be brown or yellow brown while at other times there was no visual evidence but simply a decrease in the reaction rate. The effect of the deposit is to reduce the light intensity, which in turn lowers the reaction rate.

Krol (37) has recommended the use of a minor amount of an additive selected from the ferrocyanides or ferricyanides of metals from Group I and II; preferably 0.035 parts by weight of potassium ferrocyanide ($K_4 Fe (CN)_6 \cdot 3H_2O$), dissolved in 1:1 parts by weight of water and 3000 parts by weight of paraffin wax, to overcome the effect of ferric chloride contaminant.

Generally chlorinated paraffin waxes are unstable at higher temperature. Thermal stability is measured in terms of the percent of the HCl evolved upon heating for 4 hours at 175°C. An addition of 0.05-2.5% of acetonitrile (methyl cyanide) was effective for stabilizing chlorinated paraffin wax against heat and light (40). In another patent (41) 0.1 to 1% (by weight) of an alkaline earth hydroxide was added to chlorinated paraffin and the mixture was heated for more than 10 minutes at 30-70°C to make a chlorinated paraffin stable to heat.

Most of the commercial chlorinated paraffin waxes have light amber, pale yellow, honey or yellow color, depending upon the percent chlorination, feed stock, chlorination temperature and flow rate of chlorine. The desired color is a clear light color (ASTM ≤ 0.5), for 45% chlorinated product. If temperature higher than 90°C is employed, the product is

off color, but nevertheless, addition of small amount of 4,4' Tetraalkyldiamino phenyl-methanes, trialkylphenols or alkylaminophenols (0.1-10 ppm based on paraffin) can be added to paraffin during chlorination, to avoid colorization (42).

Various patented processes are available, for chlorination of paraffin wax (42, 43, 44, 45, 46), but each one of them uses a particular type of paraffin wax feed, a range of chlorination temperatures and slightly different chlorine feed rate.

* * *

CHAPTER III

EXPERIMENTAL SET-UP AND PROCEDURE

A. De-Oiling:

De-oiling experiments were conducted on slack wax obtained from Barauni Refinery processing Naharkatia crude. As far as possible, commercial solvents were used.

Equipment:

A schematic diagram of the de-oiling equipment is shown in Fig. 1A., constructed of brass and mild steel, it consisted essentially of four sections:

1. A brass cylinder of 6 cms. internal diameter, 0.3 cm. thickness, and 17.5 cms. length. This had external threads at both the ends. The top end was screwed into the cylinder head, also made of brass, and the other end into a brass cone, which had a hole at the bottom, about 0.3 cms. in diameter.
2. A screw made of mild steel (1.25 cm. dia.), having external grooves, passed through the cylinder head, and had a rotating handle at the top, about 8 cms. in diameter.
3. The screw carried a piston, made of two brass plates, and in between, had a washer of Neoprene rubber to prevent the seepage of the liquid phase between the piston and the wall.

4. The brass cone, had a plate brazed to it, which had 4 cms. external threads, about 2 cms. above the apex, and this fitted exactly into a mild steel ice bath having a hole with 4 cms. internal threads at the bottom.

The brass cone top, also contained a perforated brass plate about 0.5 cm. in thickness, over which was placed a layer of thin canvas, which in turn was covered by two filter papers.

Fig. 1B shows a refining and de-colorizing equipment for the scale wax obtained after de-oiling. It simply consisted of a 4 cms. dia. glass column, about 20 cms. in length, which was packed with silica gel. The entire column was wrapped by an Electric Heating Cord (Flexotherm) of the type T1-64(a). This gave a temperature of 100°C in the middle of the column. It was found good enough to keep the molten wax flowing rapidly.

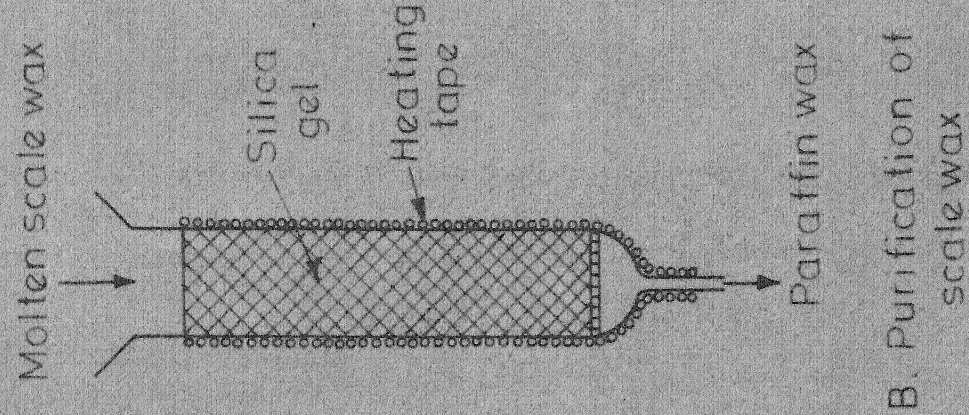
Procedure:

In the solvent de-oiling experiments, some amount of slack wax was taken in a beaker and heated until it melted. Then an equivalent amount of solvent (by weight), which was pre-cooled to the de-oiling temperature was added and the whole mass was stirred thoroughly. The wax-solvent slurry was kept in an ice bath for about half an hour to bring its temperature down to the de-oiling temperature. During this time too, stirring

was continued. After the de-oiling temperature was obtained, the wax-slurry was transferred to the brass cylinder, which was surrounded by ice or (ice + salt) mixture to maintain the de-oiling temperature. More of pre-cooled solvent was added over a span of one hour and the mass was allowed to filter. The solvent was added until the desired solvent to slack wax ratio was obtained. The slurry was sometimes stirred. The whole thing was left for about 1/2 hr., and when most of the solvent had been filtered, the screw carrying the piston was lowered inside the cylinder, and pressure was then applied by slowly turning the screw by the handle. The operation was carried out until the screw did not turn even one half a revolution, when the whole mass was left to itself for about fifteen minutes. This determined the pressing time. The de-oiled wax was taken out and weighed. Slack wax to solvent ratio was varied and the same process repeated.

The de-oiled wax thus obtained was heated to 100°C in a controlled temperature heating mantle, and air (purified by passing through a tube filled with absorbent cotton) was passed to evaporate the solvent. The wax obtained was again weighed and oil content (% by weight) was determined (discussed separately).

The de-oiled wax, known as scale wax was passed through the silica gel bed (maintained at 100°C, to avoid solidification of the wax and to improve its filterability), and refined paraffin wax was obtained.



1. Ice bath
2. Piston
3. Brass cylinder
4. Perforated brass plate
5. Brass cone with internal threads
6. Cylinder head with internal threads
7. Mild steel screw
8. Mild steel handle
9. Brass cone brazed to a brass plate with external threads

Fig. 1 - Schematic diagram of the de-oiling equipment.

B. Chlorination:

Experiments were conducted on pure paraffin wax obtained from the local market, (about 0.2% oil content by weight), wax obtained by de-oiling slack wax (scale wax) and refined scale wax. Commercial grade chlorine gas was used for all chlorination experiments.

Apparatus:

A schematic diagram of the experimental set-up is shown in Fig. 2. The apparatus consisted mainly of a reaction kettle, a rotameter, a condenser, an absorption column, cooling coil (made of Aluminium) a pyrexrespirator bottle containing sodium hydroxide solution; and a sampling device.

A "Teflon" needle valve, along with a fine adjustment valve were used to control the flow rate of chlorine gas. PVC and Tygon tubing was used for all connections.

The reaction kettle was spherical in shape, with a diameter of 15 cms. Three inlets, one for introducing chlorine gas, one for the condenser, and the last for the sampling device were provided. A thermometer pocket was also provided. The reaction kettle was kept in a water bath. This was provided with an extra cooling arrangement in the form of a helical aluminium tubing, about 0.5 cm. internal diameter, and one meter length, through which cold water was circulated.

The unreacted chlorine gas and hydrochloric acid passed through a condenser and then to an absorption column (about 10 cms. dia. and 60 cms. packed height). The column was filled with 1 cm. raschig rings. A distributor was provided at the top of the column to minimise channeling. Whatever chlorine and hydrochloric acid gases escaped this column, were passed into a respirator bottle containing strong (4N to start with) sodium hydroxide solution.

A 300 W bulb was provided as a light source to increase the reaction rate.

The chlorine gas introducing system was provided with a distributor, which distributed the gas evenly in all directions and gave good stirring too.

Procedure:

About 1 Kg of wax (pure paraffin wax, scale wax, and refined scale wax) was melted in a beaker and fed to the reaction kettle. The water bath temperature, was kept at 5°C higher than the desired reaction temperature and sufficient time was allowed for the wax to come to the reaction temperature. The teflon valve on the chlorine cylinder was opened and the flow rate was adjusted by the fine adjustment valve. For measuring the flow rate, the gas was passed through a rotameter (calibrated for chlorine with a range of 0.2 lit/min. to 2.5 lit/min.) and after the desired flow rate (0.3 lit/min.)

was obtained the chlorine gas was directed to the reaction kettle, by means of a three way valve. The fine adjustment valve was not touched after this.

The light source (300 W bulb) was put on and the reaction was started. The gases from the reaction vessel, (unreacted chlorine and hydrochloric acid), were cooled in the condenser and then sent to the absorption column. Hydrochloric acid gas was absorbed in this tower and whatever was left out, along with chlorine was adsorbed in sodium hydroxide solution.

The chlorination reaction is an exothermic reaction, and to maintain the temperature, a cooling coil was used. Whenever the reaction temperature went up by 2°C water was circulated through the cooling coil and temperature brought down. By trial and error, it was found that keeping the bath temperature 5°C below the desired reaction temperature, the reaction temperature fluctuations were minimized.

Samples were withdrawn at regular intervals of 3 hours or more and the reaction was continued until it was no longer possible to take samples, because of the increase in viscosity.

After completion of the reaction, which took generally 34 hours, the withdrawn samples were analysed for percent chlorination and other properties of chlorinated paraffin waxes, e.g. density, refractive index and viscosity.

The analysis procedures have been discussed separately.

CHAPTER IV

PRODUCT TESTING PROCEDURES

1. Determination of Oil Content (Percent by Weight) in Waxes:

The method was adapted from ASTM-IP standard No. ASTM D 721-IP 158/66 T (47), with slight modifications in the apparatus, and operating conditions.

Fig. 3 shows the schematic diagram of the apparatus, with all dimensions.

Procedure:

About 20 gms. of wax was melted in a beaker and about 1 gm of it was taken in a preheated pipette (about 1.3 ml.) and was transferred into a clean dry test tube (2.5 cm. O.D. shown in the Fig.). The weight of wax taken was measured accurately up to 4th decimal place with the help of a Mettler balance.

About 15 ml. of methyl ethyl ketone was added in the test tube, and it was heated at 60°C in a water bath until all the wax melted. The weight of the solvent was now determined after wiping and drying the outer surface of the test tube.

The test tube was plunged into a cooling bath which contained crushed ice plus common salt in the ratio of 3:1 (approximately), and the temperature obtained was -15°C. The test tube was kept for about 1/2 hour in the cooling bath, with

continuous stirring by means of a thermometer, until the temperature inside the test tube reached -10°C .

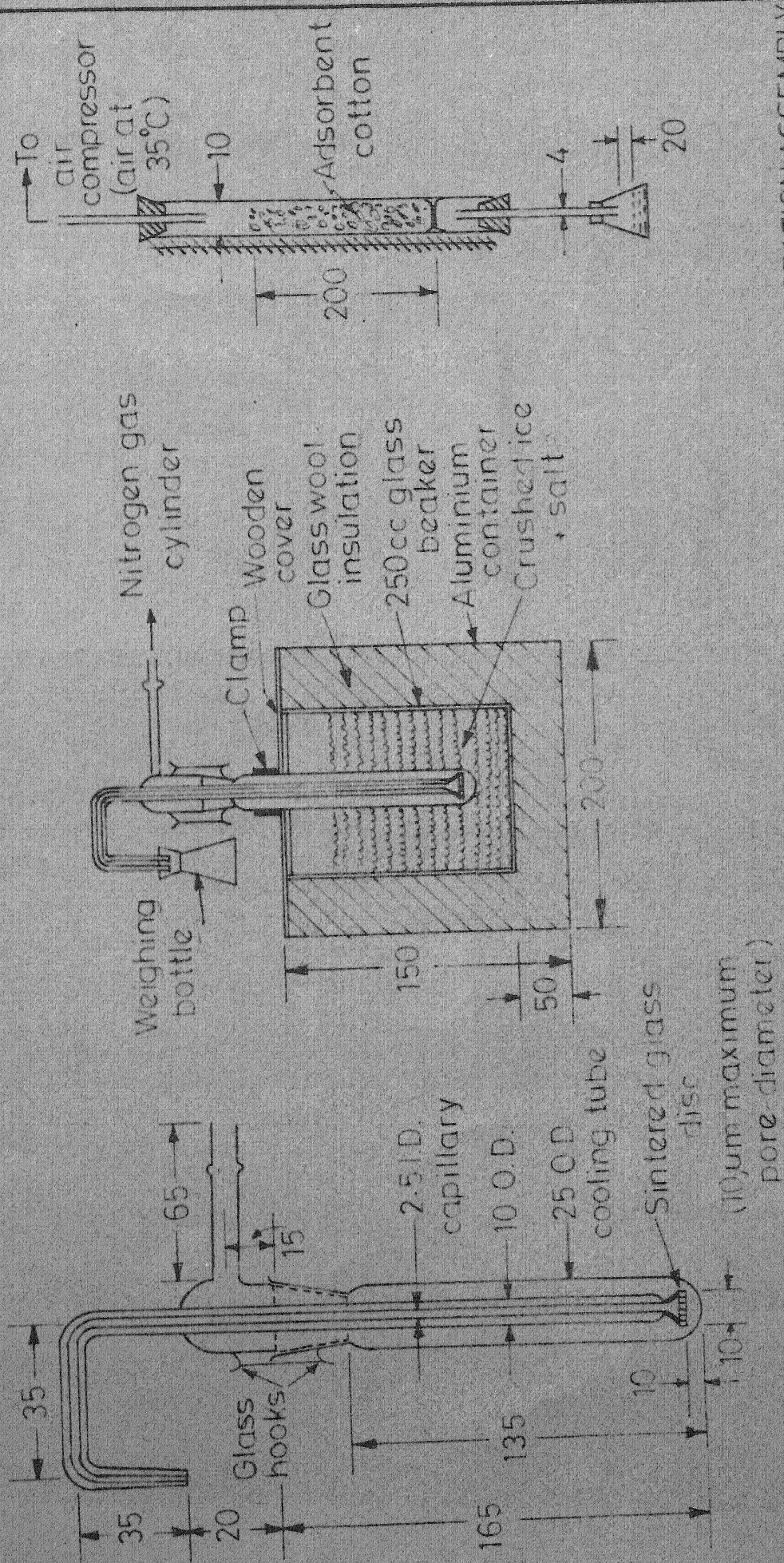
Now the clean dry filter stick was immersed in the test tube, and both were fastened by means of two springs. An unstoppered 15 cc weighing bottle, which was previously weighed together with the glass stopper, was put under the delivery nozzle of the filtration assembly. Pressure was applied to the filtration assembly and about 4 ml. of filtrate was collected in the weighing bottle. It was removed, stoppered and weighed accurately.

The weighing bottle was unstoppered and placed under the jet of the evaporation assembly. The tests were conducted in summer and temperature of air was about $34 \pm 2^{\circ}\text{C}$, which is just the temperature required, and therefore no pre-heating of air was needed. Air was supplied at 2 to 3 liters per minute. After about 30 minutes, when the solvent MEK had evaporated, the weighing bottle was removed from under the evaporation assembly and weighed.

The amount of oil in the wax was calculated as follows:

$$\text{Oil content, percent by weight} = \frac{100 \times \text{weight in gm. of oil residue} \times \text{weight in gm. of solvent (MEK)}}{\text{weight in gm. of wax sample} \times \text{wt. in gm. of solvent evaporated}}$$

A typical calculation has been shown in the Appendix A. The



EVAPORATION ASSEMBLY

COOLING BATH

FILTER STICK

All dimensions in millimeters.
(Not to scale)

Fig. 3 - Apparatus for determining the oil content in waxes.

results are precise upto $\pm 0.1\%$.

2. Determination of Melting Point (Cooling Curve Method)

The method used is described in ASTM-IP standard No. ASTM D 87/66-IP 55/67 (47),

Procedure:

The wax sample was taken in a test tube (2.5 cm. O.D. and 10 cm. in length), and was heated nearly 10 deg. above its melting point. The test tube was nearly half filled with the wax sample. It was put in another glass column (5.0 cm. O.D. and 11.5 cm. in height) which was closed at one end. This column, in turn was surrounded by water at 30°C, contained in a glass container (13 cm. I.D. and 15 cm. height). The melting point thermometer (temperature range 50-80°C with 0.1°C graduations), was inserted in the wax sample, through the centre of a cork, such that the distance between the bulb of the thermometer and the bottom of the test-tube was 1 cm.

Now the thermometer reading was noted after every 30 secs. and the test was discontinued after the wax had solidified completely. The melting point was obtained from the temperature vs. time graph.

3. Determination of Chlorine (% by weight) in Chlorinated Paraffin Waxes:

The method used was adapted from ASTM E 256-67 "Chlorine in Organic Compounds by Sodium Peroxide Bomb Ignition" (48)

and ASTM D 808-63 "Chlorine in New and Used Petroleum Products-Bomb Method" (49), with slight modifications. The above mentioned methods, do not work satisfactorily for chlorinated paraffin waxes. Infact, when the first method (E 256-67) was used, the mixture sodium peroxide and potassium nitrate did not catch fire when ignited. Therefore the ignition mixture was changed to 0.75 gm benzoic acid, 0.5 gm of sodium peroxide, 1 gm. of potassium nitrate, 0.75 gm. of sodium hydroxide and 0.5 gm. of sample. This when ignited, burnt very well, and is recommended for determining the percent of chlorination in chlorinated paraffin waxes. The method was tested on chemicals with known percent chlorination by weight e.g. chlorinated paraffins (40% chlorination), ethylene dichloride and aniline hydrochloride salt and was found to give results accurate to $\pm 1\%$.

The method is based on the fact that when chlorinated paraffin waxes are heated above 400 to 500°C, they readily give out HCl gas, which instantaneously reacts with sodium peroxide and sodium hydroxide at elevated temperatures to give sodium chloride, which can be titrated by precipitating the chloride using silver nitrate, and finding the weight of the precipitate, silver chloride.

Apparatus:

The apparatus consisted of a Parr Bomb Calorimeter (50) with the following essential parts:

1. The oxygen bomb, in which the charge was burnt.
2. The bucket containing water, in which the bomb and thermometer were immersed.
3. The outer casing of the bomb calorimeter, for protection against any violent explosion.
4. The ignition system which supplied a 4 ampere, 18 volt current through a 10 cm. length of No. 34 B and S gage nickle-chromium iron fuse wire, to ignite the charge.
5. An oxygen cylinder with a pressure regulator, supplied along with the Parr Bomb Calorimeter.

Procedure:

The charge consisting of 0.75 gm. of benzoic acid, 0.5 gm. of sodium peroxide, 1 gm. of potassium nitrate, 0.75 gm. of sodium hydroxide and 0.5 gm. of CPW sample, was taken in a metal combustion capsule. The charge was so arranged that the bottom layer consisted of 0.25 gm. of benzoic acid, above which sodium peroxide and potassium nitrate layer, then the sample followed by sodium hydroxide layer and the top layer again consisted of 0.5 gm. of benzoic acid. This was to facilitate complete burning of the charge, and to ensure that the HCl gas liberated reacts with sodium hydroxide and sodium oxide completely to give sodium chloride.

A 10 cm. fuse wire was attached to the two terminals of the oxygen bomb and it was coiled in such a way that its

coiled portion was dipping in benzoic acid. The bomb was assembled and oxygen was admitted into the bomb, until the pressure inside reached 30 atms.

The bomb was immersed in the cold water bath and covered. The contents were fired. The rise in water temperature was noted to make sure that complete combustion had taken place. The bomb was taken out of the cold water both and allowed to stand for about 1/2 hr., to ensure that the reaction was complete within the bomb.

The oxygen pressure was released and the interior of the bomb, the combustion cup and the inner surface of the bomb cover, were rinsed thoroughly with a fine jet of hot distilled water. The washings were collected in a beaker. With the combustion cup still inside the beaker, the washings were heated, and the combustion cup was washed very thoroughly with fresh distilled water.

The wash water was allowed to cool and then filtered. The filtered solution was acidified by adding HNO_3 (1:1) drop by drop until acid to methyl red. After it had neutralised the alkali, an excess of 2 cc of HNO_3 was added. Now about 10 cc of AgNO_3 (50 gm. of AgNO_3 in 1 lit. of distilled water) was added to the solution. The solution was heated to ensure complete precipitation of AgCl . After heating, it was kept in the dark for about an hour and then filtered on a weighed fritted glass filter funnel. The precipitate was dried, cooled

in a dessicator and weighed accurately.

A blank run, with no CPW sample was made and the weight of the precipitate was found out. It was very very small, 0.005 gms. Chlorine percent by weight was found by a simple formula, which is given below:

$$\text{Chlorine percent by weight} = 24.74 \frac{(\text{weight of ppt. obtained} - \text{wt. of ppt. in blank run})}{\text{Weight of CPW sample taken}}$$

A typical calculation is shown in Appendix B. The accuracy of results is estimated to $\pm 1\%$.

4. Viscosity Determination of Chlorinated Paraffin Waxes:

For measuring the viscosity of chlorinated paraffin waxes, the rotation viscosimeter RHEOTEST 2 was used, at room temperature (35°C). This gives the viscosity as a function of shear stress and shearing gradient. Thus it is possible to characterize the fluid properties of CPW's.

A typical calculation is shown in Appendix C.

5. Refractive Index of Chlorinated Paraffin Wax:

Bauch and Lomb "Abbe Refractometer" at room temperature was used to find the refractive index of liquid chlorinated paraffin waxes. For solid CPW's the temperature was maintained at 50°C to keep them in liquid state. The least count of the refractometer was 0.0001.

6. Density of Liquid Chlorinated Paraffin Waxes:

Density was determined at room temperature (35°C) using a density bottle.

* * *

CHAPTER V

SELECTION OF DE-OILING SOLVENTS

To start with, certain basic criteria were laid down for a prospective good solvent. The solvent must not possess a corrosive action, it should not be highly poisonous, it must be volatile with steam, and easily separable from water and must not react with water. It must be miscible with the oil in any ratio at 30°C and must still dissolve the oil readily at -30°C (10). A good de-oiling solvent should also have the lowest solubility for wax, since a solvent of low wax solubility will permit de-oiling at higher temperatures, with consequent saving in refrigeration costs. And finally since the de-oiled wax is to be removed by filtration, the solvent should have a high filtration rate. And above all this, the solvent should be easily available at reasonable cost.

The most common de-oiling solvent used until 1965 was MEK. But the modern plants that are coming up now a days are adopting the Edeleanu process, which employs ethylene dichloride as solvent. As mentioned earlier in Chapter II, lot of research has lately been done on higher ketones as de-oiling solvents.

In nutshell, most of the solvents mentioned in Chapter II meet other requirements, such as stability, non-corrosiveness, reasonably lower boiling points and low water solubility. The only criteria that remain of importance are the wax solubility

and the solvent cost. Table 3 gives the solubility of paraffin wax in different solvents considered and their approximate costs.

TABLE 3

Solubility of Paraffin Wax in Various Solvents and
Approximate Cost of Solvents

Solvent	b.pt. °C	Solubility of Wax, gm. of wax		Ref.	Price in Rs/Kg.	Ref.
		Temp. °C	100 gms. of solvent Solubility			
1. Heavy Naphtha		20	20			
		10	8	(51)	4.00	(55)
		0	3			
2. Light Naphtha		20	35			
		10	9	(52)	4.00	(55)
		0	4			
3. MEK	79.57	20	0.3			
		0	0.1	(53)	10.00	(55)
		-10	0.02			
4. Methylene Dichloride	39.8	20	1.5			
		10	0.06	(54)	6.00	(56)
5. Ethylene Dichloride	83.5	20	1.0			
		10	0.04	(51)	3.20	(56)
6. Turpentine (150-175)		20	19.0			
		10	5.0	(52)	1.95	(56)
		0	4.0			
7. MIBK	112.9	10	1.0			
		0	0.2	(53)	5.50	(56)
		-10	0.04			

A critical look at Table 3, would reveal, that heavy naphtha, light naphtha and turpentine are no good as solvents, because of high solubility of wax at 0°C, as compared to other solvents. One may argue that we are losing only 4 percent of wax, but taking the overall economics of the de-oiling process, even 0.5% of wax in the lubricating oil, causes it to gel at 10-20°C (10) and increases the pour point to 5-6°C (17), and the oil can no longer be used as lube oil. In case we want to recover the lube oil, we have to dewax it, using a better solvent.

The other solvent MEK, although the best, as far as low solubility of wax is concerned, is not economical, firstly because of high cost and secondly because of increased solvent losses during de-oiling (low b. point. and high vapor pressure at de-oiling temperature).

The remaining solvents MIBK, ethylene dichloride, (ethylene dichloride plus methylene dichloride, 1:1 by weight) were investigated in detail.

* * *

CHAPTER VI

RESULTS AND DISCUSSION

A. De-Oiling of Slack Wax:

The slack wax obtained from Barauni Refinery contained 13.6% by weight of lubricating oil. Its drop melting point was in the range of 55-60°C, indicating the presence of paraffin waxes; because the melting point of micro-crystalline wax is above 75°C (18). It was de-oiled using three different selected solvents, as already discussed in Chapter IV.

The results of laboratory de-oiling experiments are given in Figures 4(a) to 4(c) and Table 4. In general the following behaviour has been observed.

1. The oil content in scale wax decreased as the solvent to slack wax ratio increased.
2. The yield of scale wax decreased as the solvent to slack wax ratio increased.
3. The retention of solvent in de-oiled wax increased initially, but after a certain oil content was reached, it started decreasing.
4. The pressing time decreased as the solvent to slack wax ratio was increased.

A glance at Fig. 4(a) would reveal, that using 3 times by weight of MIBK gave a de-oiled scale wax containing approximately 0.5% by weight of oil, while to get the same

quality of scale wax using Ethylene Dichloride and Ethylene Dichloride + Methylene Dichloride, the required ratio was greater than 7. Taking the overall economics of the process (assuming 10% loss of solvent during processing and recovery), it is doubtless to conclude that MIBK, (3 times the weight of slack wax) is the best solvent. This solvent, because of its higher boiling point (112.9°C) over Ethylene Dichloride (83.5°C) will have less evaporation losses during processing, and also, the load on distillation column during solvent recovery will be much less.

As compared to MEK, the most common solvent used in de-oiling at present, MIBK has the following advantages:

1. Relatively lower cost of solvent
2. Reduction in evaporation losses due to its reduced volatility. The boiling point of MIBK is 33°C higher than MEK.

The yield of scale wax (% by weight) obtained, using 3 times MIBK, 7 times Ethylene Dichloride, and 7 times Ethylene Dichloride + Methylene Dichloride 1:1 by weight, was nearly the same (Fig. 4(b)), about 80 % by weight of slack wax. The retention of the solvents in de-oiled waxes was also comparable (Fig. 4(c)), when the above mentioned solvent to slack wax ratios were employed. It varied from 20% by weight in case of 3 times MIBK to 16% by weight in case of 7 times Ethylene Dichloride.

The melting point of scale wax using MIBK as solvent was in the range of 57-60°C, indicating thereby the presence of small amount of soft waxes, which were removed to some extent during de-oiling. This explains the difference between the theoretically expected yield of scale wax (assuming no wax lost) and actually obtained. Most of the wax that is lost during de-oiling goes along with the oil and not with the solvent. This can be seen by comparing the yield of scale wax and the final oil content, when the solvent to slack wax ratio is increased. Thus the major part of wax lost during de-oiling is because of its higher solubility in oil, rather than in solvent.

The retention of solvent in de-oiled wax increased as the solvent to slack wax ratio was increased (Fig. 4(c)) but after a certain oil content was reached in the scale wax, it started decreasing. Although the reason for this behavior is not clear at this stage, one possible explanation can be given in terms of the amount of solvent retained by the oil, interfacial forces at play and the wettability of wax. In case of solvent: slack wax ratio =1, enough solvent is not available to completely wet the wax and it is preferentially retained by the oil. As more and more solvent is added, the wax retains more of it, and after a certain oil content, when the wax is completely covered by solvent film, any further removal of oil decreases the solvent (weight %) retained in the de-oiled wax.

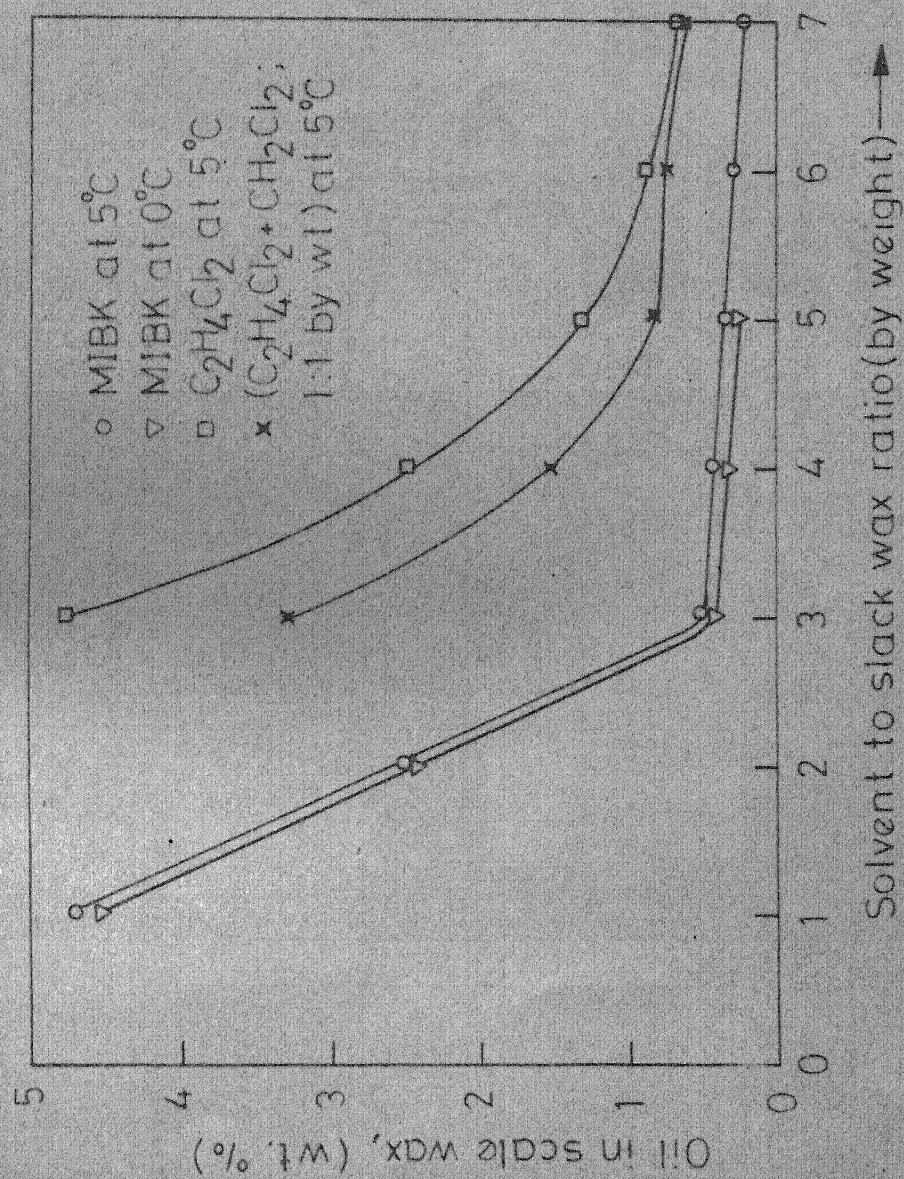


Fig.4(a) - % oil (by weight) in scale wax vs. solvent to slack wax ratio.

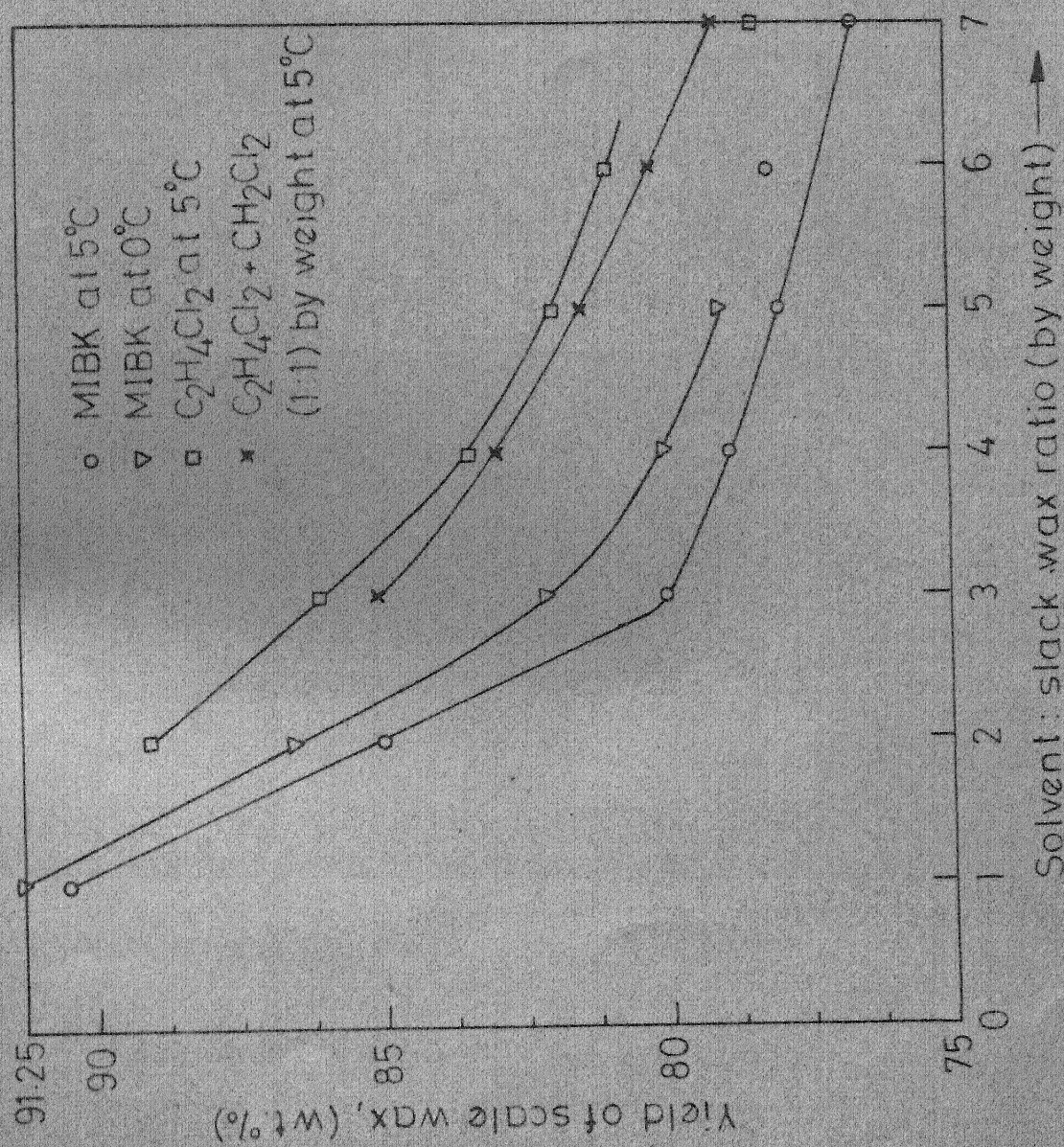


Fig 4(b)- Yield of scale wax vs. solvent to slack wax ratio.

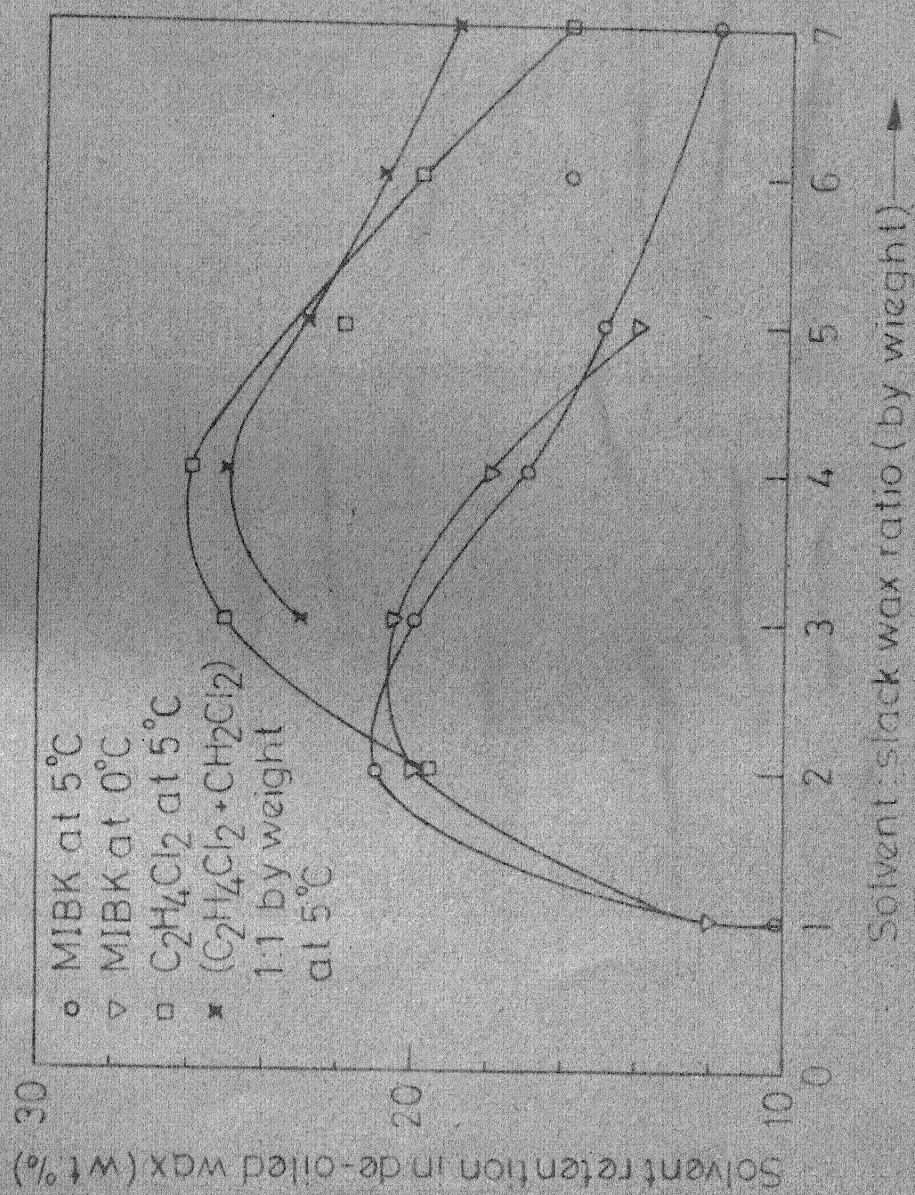


Fig 4(c) - Solvent retention in de-oiled wax vs. solvent to slack wax ratio.

TABLE 4PRESSING TIME VERSUS SOLVENT TO SLACK WAX RATIO(BY WEIGHT)Experimental Conditions:

Filtration time: One hour after adding the final
batch of solvent

Weight of Slack wax Taken: 50 gms in each experiment

Solvent: MIBK

Temperature: 5-6°C

Solvent to slack wax ratio (by weight)	Pressing Time
1	1 hr. 20 minutes
2	1 hr. 10 minutes
3	50 minutes
4	40 minutes
5	35 minutes
6	30 minutes

Finally, the pressing time decreased as the solvent to slack wax ratio increased (Table 4(a)). This is explained, if we look at the wax crystallization that is occurring during chilling. It is well known that wax crystallizes in plates and needle forms and the difference in the rates of crystallization is attributed to the presence of soft wax and oil in the medium. The presence of oil increases the viscosity of the medium, and increased viscosity retards crystallization. And also soft waxes crystallize in needle form, while higher melting point waxes crystallize in plate form. The presence of low melting waxes retards the crystallization of higher melting waxes. Thus, as more and more of oil and soft waxes are removed from the medium, wax crystallization becomes faster and faster and it becomes relatively difficult to press. And since the pressing time was chosen as the time when the de-oiling mass left to itself for fifteen minutes did not allow the piston to penetrate even $1/16$ of an inch, it is concluded that because of enhanced rate of wax-crystallization at higher solvent to slack wax ratio, the pressing time decreases.

B. Chlorination of Waxes:

Scale wax obtained from de-oiling slack wax (using 3 times MIBK as solvent), having melting point $57-60^{\circ}\text{C}$ and an oil content of 0.5% by weight and scale wax purified by passing through silica gel, were chlorinated at temperatures $75 \pm 2^{\circ}\text{C}$ and $85 \pm 2^{\circ}\text{C}$, at a fixed chlorine flow rate of 0.3 lits./min.Kg.

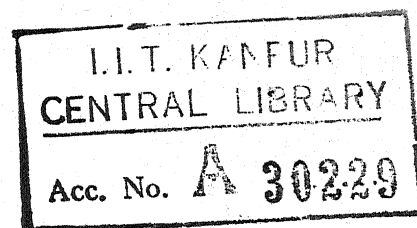
of wax. Pure grade paraffin wax (Melting point 58-59°C, oil content 0.2 by weight) was also chlorinated for comparison purposes. In each experiment 1 Kg. of wax was taken in a 2 lit. round bottom flask and chlorine was passed at the above mentioned flow rate (semibatch reaction). In one of the runs Barium stearate (10 gms./Kg. of wax), was used as a catalyst.

The results obtained are shown in Figures 5(a) to 5(e).

Samples containing less than 9 percent chlorine were partially solid at 35°C and were not studied further for viscosity, refractive index and density. More samples were taken at regular intervals, until it was not possible to withdraw, the samples quickly, because of increased viscosity and limitations of the sampling device. Each sample was studied for its chlorine content, density, refractive index and viscosity.

The rate of chlorination was fast in the beginning, until the chlorine content reached 25 to 30% by weight and after this, it retarded. While chlorinating pure paraffin wax at 85°C, it was found, that 25% chlorine content reached after 12 hrs., 32% after 18 hrs. and 49% after 34 hrs. It took about 26 hrs. for the chlorine content to reach 40% (Fig. 5(a)).

Chlorinating the same wax at 75°C, it was found that the chlorination rate was slower (as compared to 85°C), but the color of the chlorinated paraffin wax (CPW) produced was much better. When chlorinating at 85°C, the color of various



samples varied from light yellow to deep caramel with increasing chlorine content, while at 75°C it varied from light yellow to light caramel color. This difference in color is reflected in difference in refractive indices of CPW of same chlorine content (Fig. 5(d)).

Scale wax, when chlorinated at 85°C, gave CPW with very bad color, varying from light yellow to nearly black (40% chlorine content). While the same scale wax, when chlorinated, after purifying by passing through a bed of silica gel, gave products comparable to the one's obtained by chlorinating pure paraffin wax at 75°C, except for slight deterioration in color (Fig. 5(d)). The rate of chlorination of scale wax at 85°C was slower than that of pure paraffin wax at the same temperature, while the chlorination of purified scale wax at 75°C, nearly followed the (chlorine contents versus time) curve for pure paraffin wax at 75°C. It can be postulated, that at lower temperature the impurities do not affect the rate of reaction.

CPW obtained by chlorinating pure PW at 75°C in presence of Barium stearate as catalyst had excellent color starting from white (5% chlorine by weight), light yellow (35% chlorine by weight) to very light caramel color (44% chlorine by weight). The rate of reaction was also enhanced and a CPW of 40% chlorine by weight was obtained in 24 hours, as compared to 36 hours without using the catalyst.

When waxes were chlorinated without catalyst, a type of foam was observed, which was conspicuously absent while chlorinating with the catalyst (Barium stearate). This probably explains why the reaction rate goes up while using the catalyst. No possible mechanism involving the reaction of Barium stearate $\text{Ba}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$ with chlorine or HCl to give chlorine radical can be given with certainty, but a qualitative explanation saying, that the foam comes in the way of effective transmittance of light, thus retarding the reaction. In the absence of the foam, effective light transmitted increases, thus increasing the concentration of chlorine radicals in the reaction vessel and ultimately the reaction rate.

Ramage and Eckert (57), while chlorinating n-dodecane have given the rate of formation of an alkyl chloride, which can be expressed by a power law model.

$$r_a = k_a (\text{Cl}_2)^j (\text{RH})^m (\text{I})^h$$

where r_a = reaction rate

k_a = reaction rate constant

(Cl_2) = Chlorine concentration

(RH) = Hydrocarbon concentration

(I) = Intensity of light

j = reaction order for chlorine

h = reaction order of light intensity

m = reaction order for hydrocarbon

The foam that is formed decreases the intensity of light (I) inside the reaction vessel, thus decreasing the reaction rate.

The viscosity of CPW obtained by chlorinating at 85°C was significantly higher than that obtained at 75°C. At 40% chlorine by weight, the viscosity ranged from 225 to 300 centistokes. This compares well with the chlorinated paraffin (40% chlorine by wt) from Amrut Industries, Bombay which had viscosity of 375 centistokes.

While working on RHEOTEST II to find the viscosity of CPW, shear rate was changed and the corresponding shear stress was noted (Appendix C). Shear stress was plotted against shear rate (Fig. 5(c)) and it was found that the plots are straight lines, thereby indicating that the CPW is a Newtonian fluid in the range studied. Two plots for CPW (35% chlorine by weight) and CPW (25% chlorine by weight) do not pass through the origin. This is because, much reliance can not be put on the noted shear stress for low shear rates, because of equipment limitations. This is illustrated in Appendix C, where for the same shear rate at "increasing" and "decreasing" speeds, the values of shear stress differ widely, for low shear rates only.

Refractive indices of chlorinated paraffin wax (same percent chlorine by weight) changed sharply with slight deterioration in color (Figure 5 (d)). This fact can be exploited to label CPW's with ASTM color index, by just knowing their

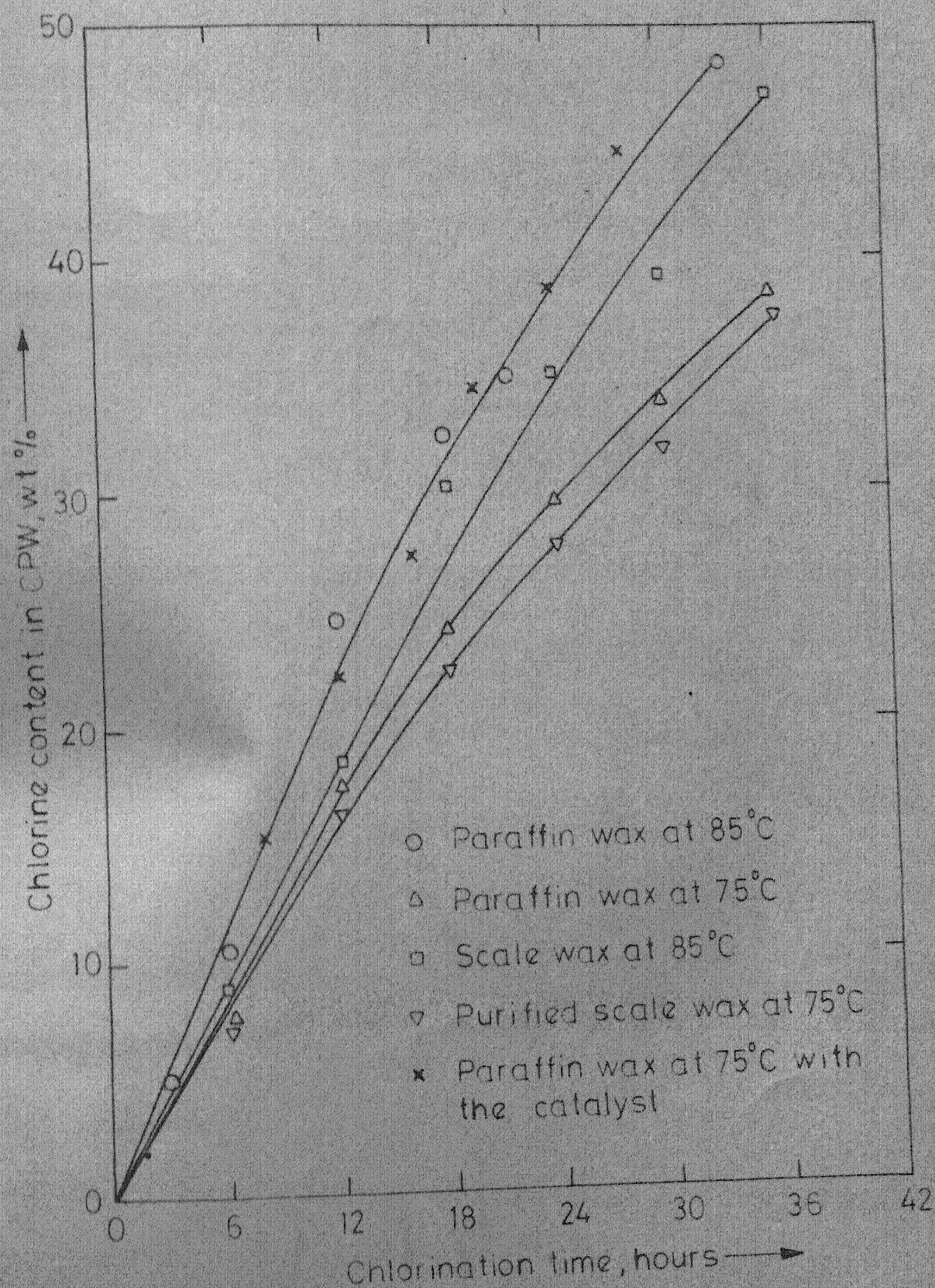


Fig 5(a)-Chlorine content in CPW, wt % vs. chlorination time at different temperature.

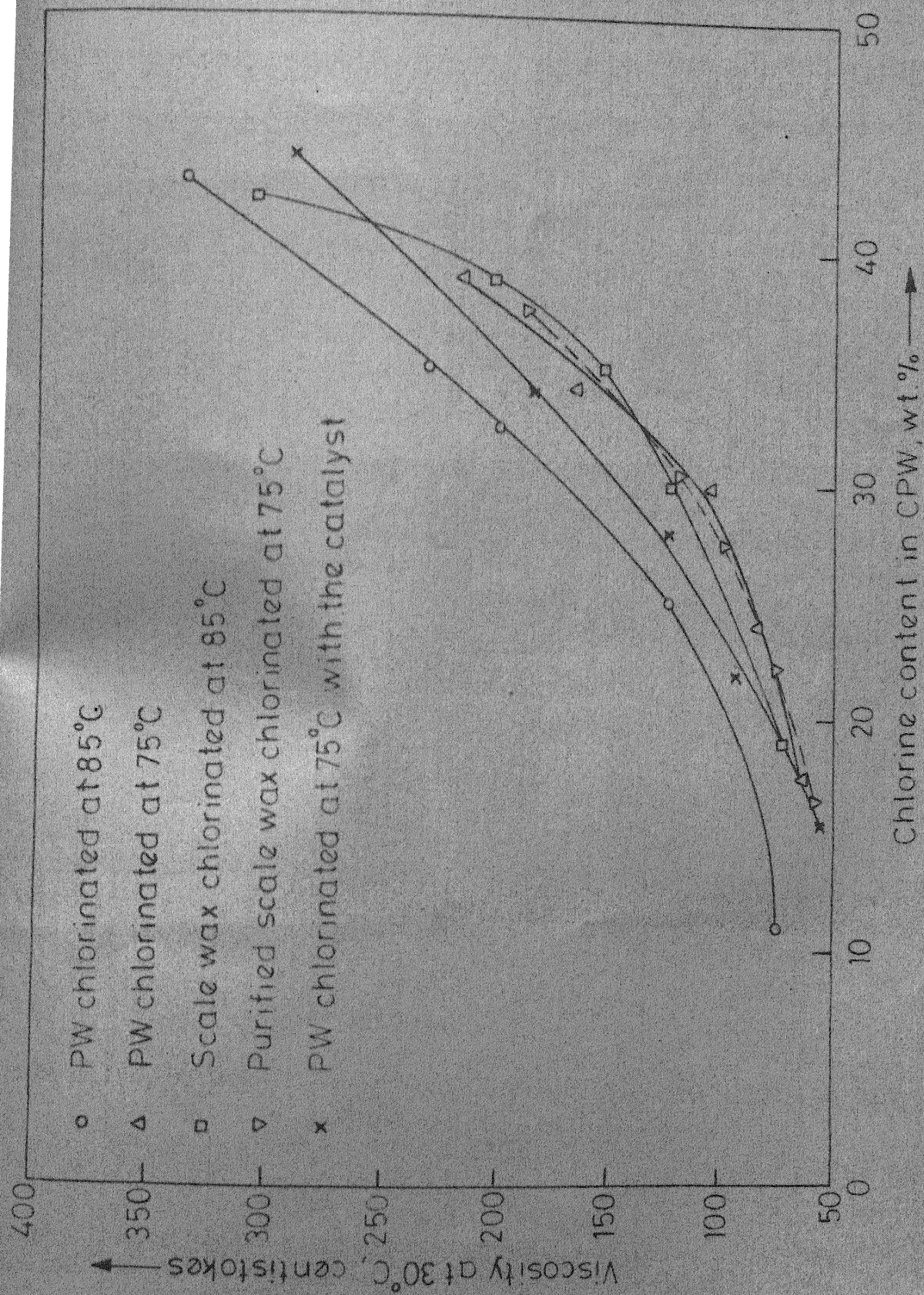


Fig 5(b) - Chlorine content (% by wt) in CPW vs. viscosity

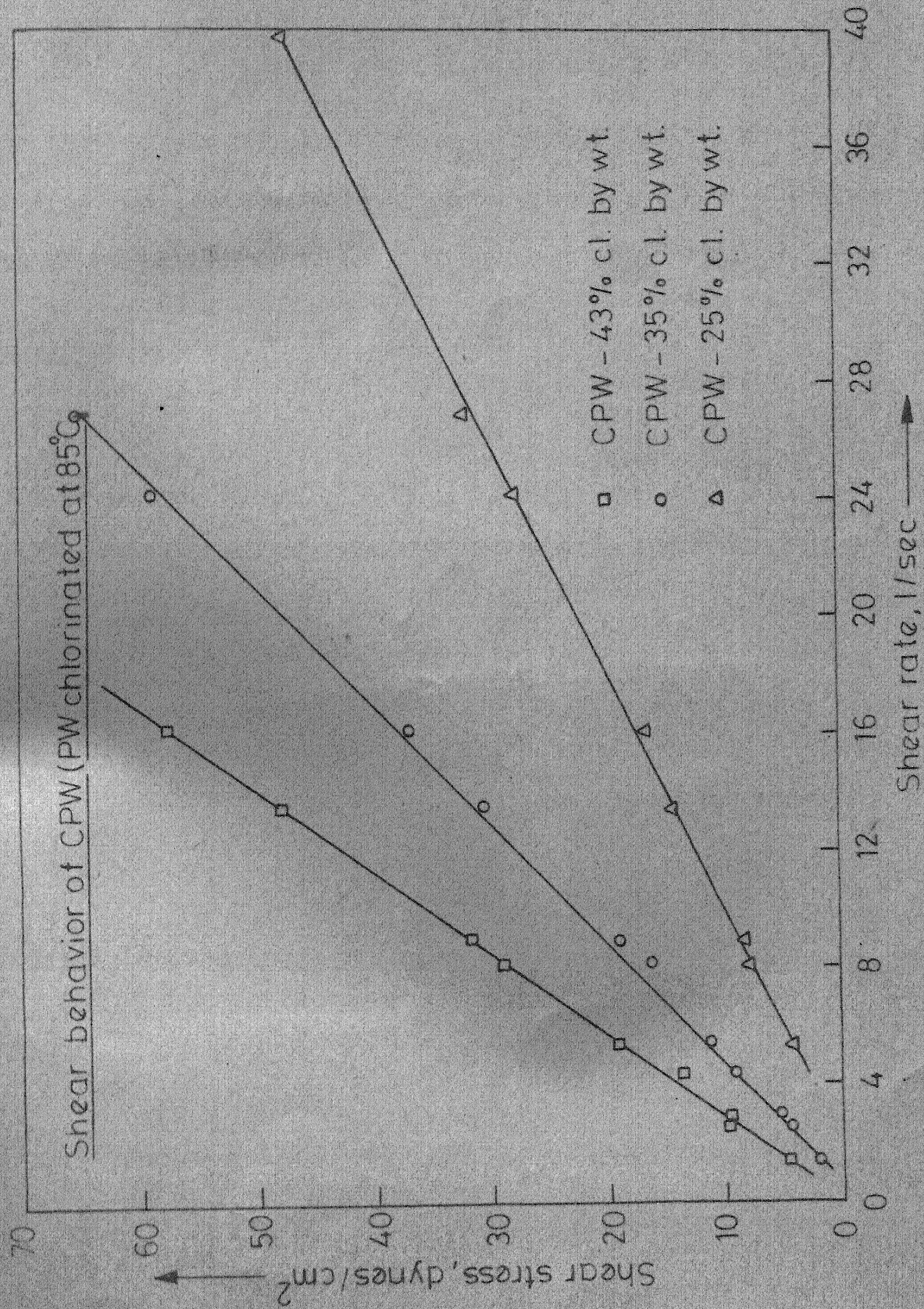


Fig.5(c) - Shear stress vs. shear rate of CPW.

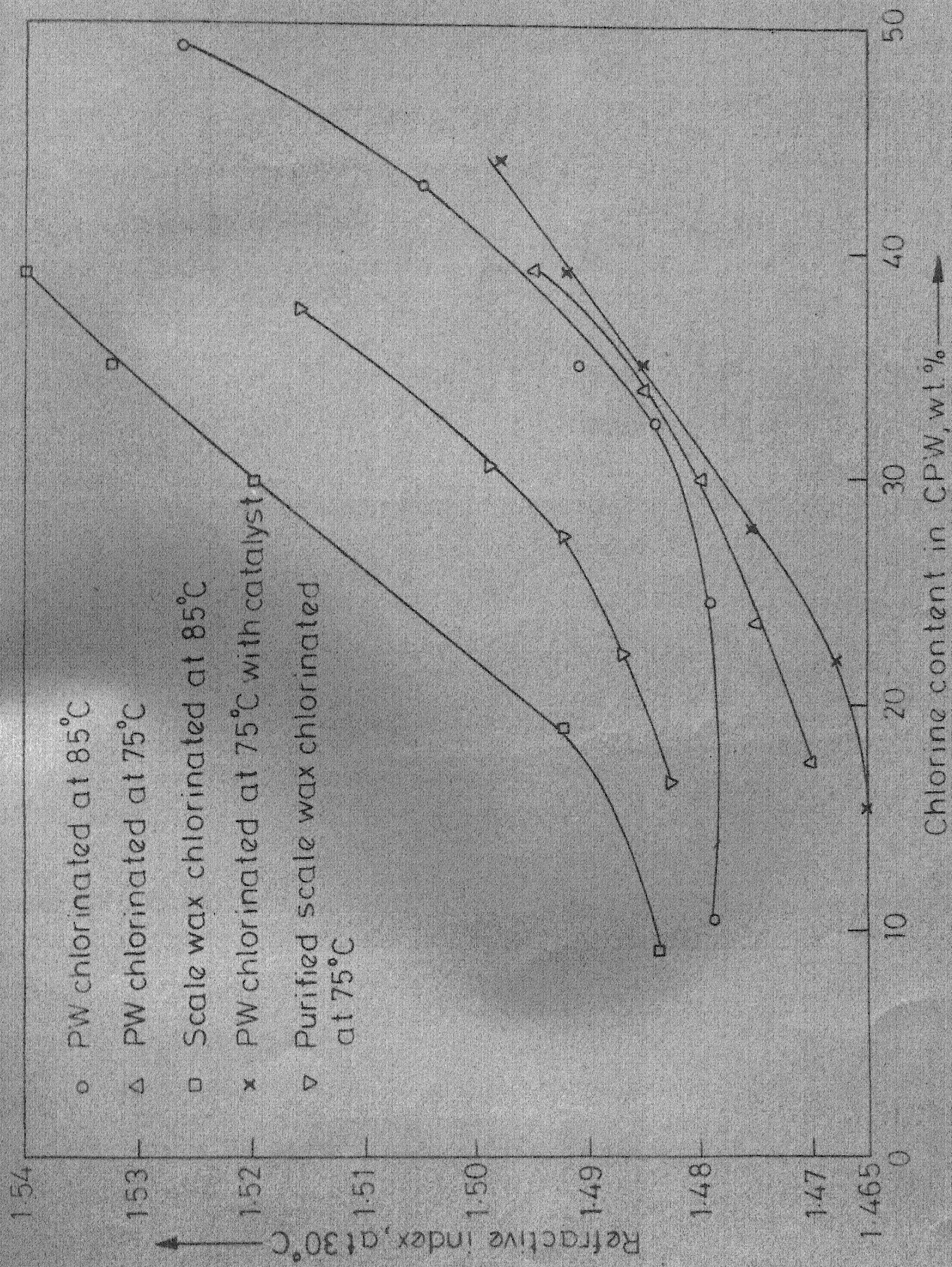


Fig.5(d) -Chlorine content (% by wt) in CPW vs refractive index.

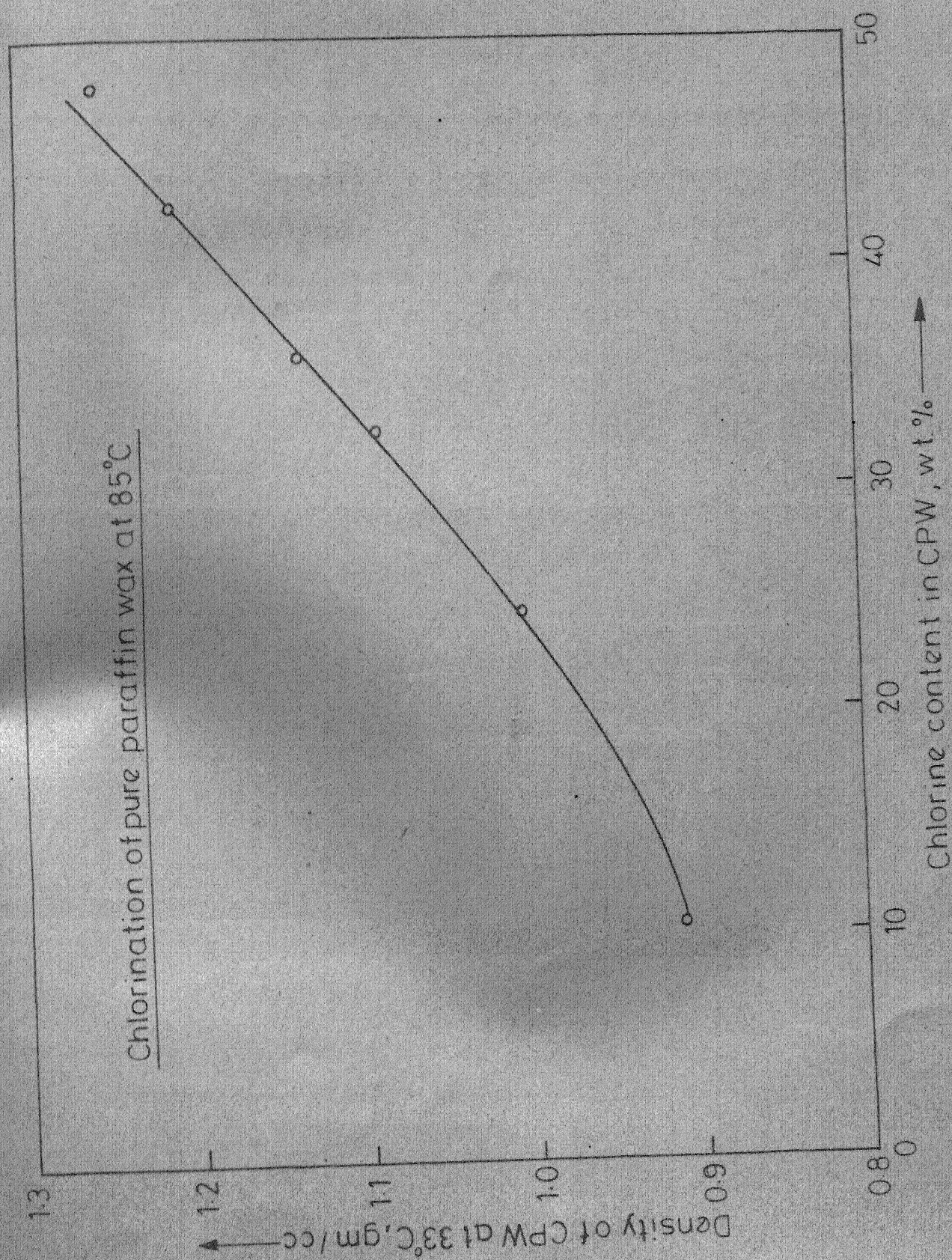


Fig 5 (e) - Chlorine content in CPW wt % vs. density.

refractive indices.

The density of CPW increased on chlorination (Fig. 5(c)). This property makes it possible to estimate the chlorine content of the CPW by just determining their densities, provided the starting PW has the same density, molecular weight and melting point. Density is not a function of chlorination temperature or flow rate of chlorine.

* * *

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

A. DE-OILING:

The following conclusions can be drawn from the studies on de-oiling of slack wax:

1. A laboratory scale de-oiling equipment has been fabricated for removing oil from slack wax using solvents at different temperatures.
2. Three times by weight of MIBK gives a scale wax containing 0.5% oil by weight, while to get similar scale wax using Ethylene Dichloride and Ethylene Dichloride + Methylene Dichloride, the required weight of solvent is more than 7 times the weight of slack wax.
3. The yield of scale wax obtained is 80% by weight of slack wax.
4. The solvent retention in de-oiled wax is of the order of 20 percent by weight of de-oiled wax and has to be extracted by distillation.

B. CHLORINATION:

1. The rate of chlorination is fast in the beginning until the chlorine content reaches 25 to 30% by weight and after this it retards.
2. The chlorination rate increases with temperature but the color of CPW deteriorates at higher temperature.

3. The catalyst Barium stearate, not only increases the rate of reaction but also brings about an improvement in color of the product.
4. For good colored CPW, the recommended temperature is 75°C and the reaction should be carried out in presence of the catalyst.
5. Small impurities in the wax do not influence the reaction rate very much but give rise to a deterioration in color of the product.
6. The chlorinated paraffin wax (upto 43% chlorine by weight) behaves like a Newtonian fluid, its viscosity being in the range of 225 to 300 centistokes and density about 1.2 at 40% chlorination.

RECOMMENDATIONS:

A. DE-OILING

1. Studies should hbe made on the usage of lubricating oil obtained during solvent de-oiling. Different pour point depressants should be tried and dewaxing of the oil can also be carried out if necessary.
2. The scale wax obtained during de-oiling should be further purified by giving it acid and clay treatment.
3. Scale up of the laboratory scale de-oiling equipment, (or variation of it) with vacuum filtration should be attempted.

B. CHLORINATION:

1. The author is of the opinion that chlorination rate increases with increased chlorine flow rate. However, no studies were conducted and it is suggested that chlorination be done at different flow rates.
2. Calcium Benzoate and calcium oleate can also be tried as catalysts and compared with Barium stearate.
3. Scale up of the chlorination equipment can be attempted.

* * *

APPENDIX ACALCULATION OF OIL CONTENT (% BY WEIGHT) IN WAXES

The amount of oil in the wax was calculated as follows:

$$\text{Oil content, percent by weight} = \frac{100 AC}{BD} - 0.30$$

where

A = weight in g. of oil residue after evaporating MEK

C = weight in g. of solvent after heating the wax and solvent at 65°C and dissolving all the wax

= (weight of test tube + weight of wax sample + weight of MEK) - (weight of test tube + weight of wax sample)

B = weight in g. of wax sample

D = weight in g. of solvent evaporated

= (weight of sampling bottle + weight of filtrate) - (weight of sampling bottle plus weight of oil residue)

0.30 = correction factor for the solubility of wax in the solvent at -10°C

The results are precise upto ± 0.1 percent.

Typical Calculation:

Sample: Scale wax obtained by using MIEK to slack wax ratio of 3 to 1 by wt.

$$\begin{aligned} 1. \text{ weight of scale wax taken} &= 26.5455 - 25.4485 \\ &= 1.0970 \text{ g.} \end{aligned}$$

$$\begin{aligned} 2. \text{ weight of MEK taken} &= 39.2500 - 26.5455 \\ &= 12.7045 \end{aligned}$$

$$3. \text{ weight of filtrate taken} = 10.3970 - 6.7075$$

$$= 3.6895$$

$$4. \text{ weight of oil residue} = 6.7100 - 6.7075$$

$$= 0.0025$$

$$5. \text{ weight of MEK evaporated} = 3.6895 - 0.0025$$

$$= 3.6870$$

$$\text{oil \% by weight} = \frac{0.0025 \times 12.7045}{3.6870 \times 1.0970} \times 100 - 0.3$$

$$= 0.52 \%$$

The above analysis when repeated gave an oil content of 0.47%.

In other tests for determining oil content in scale wax (oil content as high as or greater than 4 percent) two successive analysis differed by about 0.1 and therefore the maximum error can be taken to be ± 0.1 .

* * *

APPENDIX BCALCULATION OF CHLORINE CONTENT IN CPW (48)

Chlorine content (wt.%) in CPW was calculated as follows:

$$\text{Chlorine (wt. \%)} = 24.74 \times \frac{(\text{wt. of ppt. obtained} - \text{wt. of ppt in blank run})}{\text{wt. of CPW sample}}$$

Weight of ppt. in blank run: The charge consisted of:

Benzoic acid = 0.75 g.

Sodium peroxide = 0.5 g.

Potassium Nitrate = 1.0 g.

Sodium hydroxide = 0.75 g.

Weight of ppt. obtained = 0.005 g.

Estimation of Accuracy:

Sample	Theoretical Chlorine content (wt. %)	Experimental Chlorine content (wt.%)
Aniline Hydro- chloride Salt $\text{C}_6\text{H}_5\text{NH}_2\text{HCl}$	27.4	26.8 (-0.6)
Ethylene Dichloride $\text{C}_2\text{H}_4\text{Cl}_2$	71.6	70.7 (-0.9)
CPW(40% chlorination) from Amrut Industries	40.0	39.5 (-0.5)

Accuracy estimated about $\pm 1\%$

Sample Calculations:

wt. of sample taken = $12.1625 - 11.6485 = 0.5140$ g.

wt. of ppt. obtained = $56.8065 - 56.0580 = 0.7485$ g.

$$\begin{aligned} \% \text{ chlorination (by wt.)} &= 24.74 \times \frac{(0.7485 - 0.005)}{0.5140} \\ &= 35.5\% \\ &\text{---} \end{aligned}$$

APPENDIX C

CALCULATION OF VISCOSITY OF CPW

Viscosity Data

Test Sample: CPW (35% chlorine by weight), obtained when pure PW was chlorinated at 85°C.

Temperature: 30°C

Test	Speed Stage	Shear Stress Scale Reading (α)			Shear stress (dyne/cm ²) = Z x mean value of α	Shear Rate 1/sec. shear stress/ shear rate.	Viscosity (Poise) = shear stress/ shear rate.
		Increas- ing speed	Decreas- ing speed	Mean value of α			

I							
Z=3.17	1.b	1.0	0.5	0.75	2.38	1.5	1.58
	2b	2.0	1.0	1.15	4.76	2.7	1.77
	1a	2.2	1.2	1.70	5.40	3.0	1.78
	3b	3.3	2.5	2.90	9.20	4.5	2.04
	2a	4.0	3.4	3.70	11.40	5.4	2.16
	4b	5.2	5.0	5.10	16.20	8.1	2.00
	3a	6.1	5.3	5.95	18.80	9.0	2.10
	5b	10.5	9.5	10.00	31.70	13.5	2.34
	4a	12.2	11.5	11.85	37.50	16.2	3.32
	6b	19.1	18.0	18.60	59.20	24.3	2.20
	5a	21.0	20.0	20.50	65.00	27.0	2.40
	7b	32.0	30.8	31.40	100.00	40.5	2.48
	6a	38.5	36.8	37.60	119.00	48.6	2.43
	8b	58.8	56.2	57.50	182.00	72.9	2.48
	7a	65.2	63.0	64.1	204.00	81.00	2.50
	9b	97.5	94.0	95.7	304.00	121.5	2.50

II

Z = 32.1

	8a	11.8	11.2	11.50	370.00	145.8	2.52
	10b	17.5	17.0	17.25	555.00	218.7	2.52
	9a	19.1	18.8	18.95	610.00	243.0	2.50
	11b	29.0	28.1	28.55	915.00	364.5	2.50
	10a	34.5	33.8	34.20	1100.00	437.4	2.51

Mean viscosity = 250 centipoise (for shear rate 72.9 to 437.4/sec)
Density of 35% chlorine content CPW = 1.102

Kinematic viscosity = $\frac{\text{viscosity}}{\text{density of CPW}} = \frac{250}{1.102} = 229$ centistokes

...

APPENDIX DECONOMICS OF THE PROCESSA. De-Oiling:

Basis: 1 ton of slack wax/day de-oiled

1. Raw Material Cost:

1 ton slack wax Rs. 500/-

3 ton of MIBK (10% lost) Rs.1650/-

2. De-Oiling Processing Cost:

Heating, Chilling, Filtering, Pressing and distillation

Rs.250/ ton of slack wax

Purifying scale wax (Acid and clay treatment)

Rs. 40 (Rs.50/ton of scale wax)

Cost of pour point depressent (Para flow) to lubricating oil

= 1 Kg paraflow/100 Kg. of lubricating oil

= 1.3 Kg. = Rs.25.00

3. Salaries and Other Operating Expenses:

1 Engineer = Rs.50/day

3 Operators = Rs.60/day

Other helping staff= Rs.190/day

Total outflow of cash = Rs.2765

4. Return on Product:

Value of PW = Rs.2400 (Rs.3/Kg)

Value of lubricating oil = Rs.1300 (Rs.10/Kg)

5. Profit per day = Rs.935/day

= 280,500/year (300 days/year)

REFERENCES

1. Dean, J.C.; Chemical and Engg. News; 23(13) p.116 (1945).
2. C.A. 76, 128,997s (1972).
3. C.A. 76, 128,999 u (1972).
4. C.A. 78; 112,972k (1972).
5. C.A. 78; 112,968 p (1973).
6. C.A. 78; 112,375t (1973).
7. Saraf, D.N. and Singhal, A.K., "A Project Report Submitted to N.C.S.T." (1972).
8. Gupta, D.K.; "IICHe Seminar on Organic Chemical Industries" held at SRIIR, New Delhi in 1971.
9. Kalichevsky, V.A.; Ind. Eng. Chem. 38,p.1009-12 (1946).
10. Asinger, F.; "Paraffin Chemistry and Technology", Pergamon Press, p.47 (1968).
11. Edwards, R.T.; Pet. Refiner 36(1)p 150 (1957).
12. Pyhalae, E.; Pet. Refiner 9 (9) p.42-8 (1930).
13. David, R.A. and Huemmer, P.M.; Pet.Refiner 43(4) p.174 (1947).
14. C.A. 61 510 (1964).
15. Konstas, A.K.; Pet. Refiner 36(9) p.241 (1957).
16. C.A. 76 143166p (1972).
17. Kalichevsky, V.A. and Kobe, K.A.; "Petroleum Refining with Chemicals", Elsevier Publishing Co.p.433 (1956).
18. Rautschka, R.; Pet.Refiner 36(3) p.165 (1957).
19. Kirk and Othmer, "Encyclopedia of Chemical Technology", Interscience Publishers, Vol. 5, p.232-236 (1964).

20. Williams, R.T., Donald, S.B. and Donald, V.N.; Ind. Eng. Chem. 47(6) p.1218 (1955).
21. C.A. 61 9340f (1964).
22. Fischer, Werner; Pet. Refiner, 36(9) p.236 (1957).
23. C.A. 59 2577d (1963).
24. C.A. 70 108092r (1969).
25. C.A. 72 134,952g (1970).
26. Warnecke, J.G. and Backlund, P.S.; Pet. Refiner 37(4) p 189 (1958).
27. C.A. 76 143166p (1972).
28. C.A. 78 161873n (1973).
29. Nelson, W.L., "Petroleum Refining Engineering", McGraw Hill Book Co., p.394 (1958).
30. Mills, I.W.; Glenolden Pa., and Harvey T.W.; U.S. 3,369,993 (1968).
31. C.A. 72, 34122t (1970).
32. Anonymous; Pet. Refiner 39(9) p.275 (1960).
33. Anonymous; Chemical Engineering; 67(6) p.90 (1960).
34. Jenny, J.W. and Rahm, R.C.; U.S. 2,941,013 (1960).
35. C.A. 53, 19841e (1959).
36. C.A. 48 9055f (1954).
37. Krol, J.E., Township, M. and Henderson, A.J.; U.S. 3,467,610 (1971).
38. Hull, C.M. and d'Ouville, E.L.; U.S. 2,403,179 (1946).
39. Ziolkowski, D., Cassano, A.E. and Smith, J.M. Am. Inst. of Chem. Engg. Journal, 13 (5) p.1025 (1967).

40. C.A. 77 4857r (1972).
41. C.A. 76 126359m (1972).
42. C.A. 77 4856 w(1948).
43. C.A. 42 2098e (1948).
44. C.A. 54 p8062 u (1960).
45. C.A. 55, 21570d (1961).
46. C.A. 76 112657v (1972).
47. Indian Standard(IS: 4654-1968)" Specification for Paraffin Wax"; Indian Standards Institution, p.9 (1968).
48. ASTM E256-67, 1969 Book of ASTM Standards, Part 22, p.586(1964).
49. ASTM D808-63; 1965 Book of ASTM Standards, Part 17, p.331 (1965).
50. Parr Instrument Company; Manual No.130" Oxygen Bomb Calorimetry and Combustion Methods"
51. Poole, J.W.; Ind. Eng.Chem. 21(11) p.1098 (1929).
52. Ibid, 23(2), p. 170 (1931).
53. Tiedje, J.L.; Pet. Refiner 34(2) p.151 1955).
54. Charlisle, P.J.; Ind. Eng. Chem. 24(4) p.385 (1931).
55. Chemical Weekly, p.42 (June 23, 1973).
56. Ibid, p.16 (June 16, 1973).
57. Ramage, M.P. and Eckert, R.E., Ind.Eng. Chem. Des. Develop., 12(3) p. 249 (1973).

expected cost of plant = Rs.5 lakh

6. Depreciation = Rs.50,000/year
7. Taxable Income = 280,500 - 50,000 = Rs.230,500
8. Tax, 60% on taxable income = 1.39 lakh
9. Net Income = Rs.91500/year
10. Pay out period = 5.5 or nearly 6 years
- Rate of return = 18.3%

CHLORINATION:

Basis: 1 ton of PW/day, for 250 days a year*

1. Raw material cost

1. ton of PW = Rs.3000.00

Amount of chlorine required = 28 x 30 (28 Kg/hr-ton of wax,
for 30 hrs.)
= 840 kg.

Cost of chlorine = 840 x 1.6 (Rs. 1.6/Kg.)
= Rs.1344.00

2. Processing Cost = Rs.200/ton of PW

3. Salaries and other expenses = Rs. 500/day

4. Return on CPW

Weight of CPW produced = 1.6 tons

Value of CPW = 6400 (Rs. 4/Kg)

5. Total Profit = Rs.1056/day
= Rs.2.62 lakhs/year

expected cost of plant = Rs.3 lakh

6. Depreciation = Rs.30,000/year

7. Taxable Income = Rs.2.32 lakhs/year

8. Tax, 60% on taxable income = Rs.1.4 lakhs/year

9. Net Income = Rs.0.92 lakhs/year

10. Pay out period = Maximum 4 years

Rate of Return = 30.5%

*Chlorinating PW at 75°C, in presence of the catalyst, takes only 26 hours for the chlorine content to reach 40% by weight. Giving allowance for scale up and emergencies, 250 tons of PW can be chlorinated per year.